

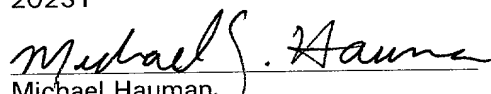
## JOINT INVENTORS

"EXPRESS MAIL" mailing label No.

EL564462485US.

Date of Deposit: August 22, 2001

I hereby certify that this paper (or fee) is being deposited with the United States Postal Service "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 CFR §1.10 on the date indicated above and is addressed to: Commissioner for Patents, Washington, D.C. 20231

  
Michael Hauman

## APPLICATION FOR UNITED STATES LETTERS PATENT

# S P E C I F I C A T I O N

---

### TO ALL WHOM IT MAY CONCERN:

Be it known that we, Michael A. Mitchell,  
a citizen of the United States of America, residing at 8805 Sweetwater  
Place, Waxhaw (28173), in the County of Union and State of North Carolina,  
and Thomas W. Beihoffer,  
a citizen of the United States of America, residing at 412 South Belmont,  
Arlington Heights (60005), in the County of Cook and State of Illinois,  
and Mark Anderson,  
a citizen of the United States of America, residing at 500 North Carlton,  
Wheaton (60187), in the County of DuPage and State of Illinois  
have invented a new and useful MULTICOMPONENT SUPERABSORBENT  
GEL PARTICLES, of which the following is a specification.

## MULTICOMPONENT SUPERABSORBENT GEL PARTICLES

### FIELD OF THE INVENTION

5 The present invention relates to multi-  
component superabsorbent gel particles containing at  
least one acidic water-absorbing resin and at least  
one basic water-absorbing resin. Each superabsor-  
bent gel particle has at least one microdomain of  
the acidic resin in contact with, or in close prox-  
imity to, at least one microdomain of the basic  
10 resin. The present invention also relates to mix-  
tures containing (a) multicomponent superabsorbent  
particles, and (b) particles of an acidic water-  
absorbing resin, a basic water-absorbing resin, or a  
mixture thereof.

15

### BACKGROUND OF THE INVENTION

Water-absorbing resins are widely used in  
sanitary goods, hygienic goods, wiping cloths,  
water-retaining agents, dehydrating agents, sludge  
coagulants, disposable towels and bath mats, dispos-  
20 able door mats, thickening agents, disposable litter  
mats for pets, condensation-preventing agents, and  
release control agents for various chemicals.  
Water-absorbing resins are available in a variety of  
chemical forms, including substituted and unsubsti-  
25 tuted natural and synthetic polymers, such as  
hydrolysis products of starch acrylonitrile graft  
polymers, carboxymethylcellulose, crosslinked poly-  
acrylates, sulfonated polystyrenes, hydrolyzed

polyacrylamides, polyvinyl alcohols, polyethylene oxides, polyvinylpyrrolidones, and polyacrylonitriles.

Such water-absorbing resins are termed

5 "superabsorbent polymers," or SAPs, and typically are lightly crosslinked hydrophilic polymers. SAPs are generally discussed in Goldman et al. U.S. Patent Nos. 5,669,894 and 5,559,335, the disclosures of which are incorporated herein by reference. SAPs

10 can differ in their chemical identity, but all SAPs are capable of absorbing and retaining amounts of aqueous fluids equivalent to many times their own weight, even under moderate pressure. For example, SAPs can absorb one hundred times their own weight,

15 or more, of distilled water. The ability to absorb aqueous fluids under a confining pressure is an important requirement for an SAP used in a hygienic article, such as a diaper.

As used here and hereafter, the term "SAP

20 particles" refers to superabsorbent polymer particles in the dry state, i.e., particles containing from no water up to an amount of water less than the weight of the particles. The terms "SAP gel" or "SAP hydrogel" refer to a superabsorbent polymer in

25 the hydrated state, i.e., particles that have absorbed at least their weight in water, and typically several times their weight in water.

The dramatic swelling and absorbent properties of SAPs are attributed to (a) electrostatic

30 repulsion between the charges along the polymer chains, and (b) osmotic pressure of the counter ions. It is known, however, that these absorption

properties are drastically reduced in solutions containing electrolytes, such as saline, urine, and blood. The polymers function much less effectively in the presence of such physiologic fluids.

5           The decreased absorbency of electrolyte-containing liquids is illustrated by the absorption properties of a typical, commercially available SAP, i.e., sodium polyacrylate, in deionized water and in 0.9% by weight sodium chloride (NaCl) solution. The  
10       sodium polyacrylate can absorb 146.2 grams (g) of deionized water per gram of SAP (g/g) at 0 psi, 103.8 g of deionized water per gram of polymer at 0.28 psi, and 34.3 g of deionized water per gram of polymer of 0.7 psi. In contrast, the same sodium  
15       polyacrylate is capable of absorbing only 43.5 g, 29.7 g, and 24.8 g of 0.9% aqueous NaCl at 0 psi, 0.28 psi, and 0.7 psi, respectively. The absorption capacity of SAPs for body fluids, such as urine or  
20       menses, therefore, is dramatically lower than for deionized water because such fluids contain electrolytes. This dramatic decrease in absorption is termed "salt poisoning."

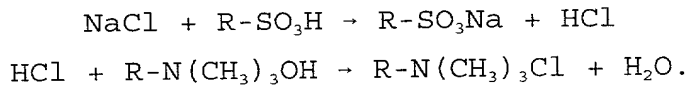
          The salt poisoning effect has been explained as follows. Water-absorption and water-  
25       retention characteristics of SAPs are attributed to the presence of ionizable functional groups in the polymer structure. The ionizable groups typically are carboxyl groups, a high proportion of which are in the salt form when the polymer is dry, and which  
30       undergo dissociation and solvation upon contact with water. In the dissociated state, the polymer chain contains a plurality of functional groups having the

same electric charge and, thus, repel one another. This electronic repulsion leads to expansion of the polymer structure, which, in turn, permits further absorption of water molecules. Polymer expansion, however, is limited by the crosslinks in the polymer structure, which are present in a sufficient number to prevent solubilization of the polymer.

It is theorized that the presence of a significant concentration of electrolytes interferes with dissociation of the ionizable functional groups, and leads to the "salt poisoning" effect. Dissolved ions, such as sodium and chloride ions, therefore, have two effects on SAP gels. The ions screen the polymer charges and the ions eliminate the osmotic imbalance due to the presence of counter ions inside and outside of the gel. The dissolved ions, therefore, effectively convert an ionic gel into a nonionic gel, and swelling properties are lost.

The most commonly used SAP for absorbing electrolyte-containing liquids, such as urine, is neutralized polyacrylic acid, i.e., typically containing 70%, and up to 100%, neutralized carboxyl groups. Neutralized polyacrylic acid, however, is susceptible to salt poisoning. Therefore, to provide an SAP that is less susceptible to salt poisoning, either an SAP different from neutralized polyacrylic acid must be developed, or the neutralized polyacrylic acid must be modified or treated to at least partially overcome the salt poisoning effect.

The removal of ions from electrolyte-containing solutions is often accomplished using ion exchange resins. In this process, deionization is performed by contacting an electrolyte-containing solution with two different types of ion exchange resins, i.e., an anion exchange resin and a cation exchange resin. The most common deionization procedure uses an acid resin (i.e., cation exchange) and a base resin (i.e., anion exchange). The two-step reaction for deionization is illustrated with respect to the desalinization of water as follows:



The acid resin (R-SO<sub>3</sub>H) removes the sodium ion; and the base resin (R-N(CH<sub>3</sub>)<sub>3</sub>OH) removes the chloride ions. This ion exchange reaction, therefore, produces water as sodium chloride is adsorbed onto the resins. The resins used in ion exchange do not absorb significant amounts of water.

The most efficient ion exchange occurs when strong acid and strong base resins are employed. However, weak acid and weak base resins also can be used to deionize saline solutions. The efficiency of various combinations of acid and base exchange resins are as follows:

Strong acid--strong base (most efficient)

Weak acid--strong base

Strong acid--weak base

Weak acid--weak base (least efficient).

5 The weak acid/weak base resin combination requires  
that a "mixed bed" configuration be used to obtain  
deionization. The strong acid/strong base resin  
combination does not necessarily require a mixed bed  
configuration to deionize water. Deionization also  
10 can be achieved by sequentially passing the electro-  
lyte-containing solution through a strong acid resin  
and strong base resin.

A "mixed bed" configuration of the prior  
art is a physical mixture of an acid ion exchange  
15 resin and a base ion exchange resin in an ion ex-  
change column, as disclosed in Battaerd U.S. Patent  
No. 3,716,481. Other patents directed to ion ex-  
change resins having one ion exchange resin imbedded  
in a second ion exchange resin are Hatch U.S. Patent  
20 No. 3,957,698, Wade et al. U.S. Patent No.  
4,139,499, Eppinger et al. U.S. Patent No.  
4,229,545, and Pilkington U.S. Patent No. 4,378,439.  
Composite ion exchange resins also are disclosed in  
Hatch U.S. Patent Nos. 3,041,092 and 3,332,890, and  
25 Weiss U.S. Patent No. 3,645,922.

The above patents are directed to nonswel-  
ling resins that can be used to remove ions from  
aqueous fluids, and thereby provide purified water.  
Ion exchange resins used for water purification must  
30 not absorb significant amounts of water because

resin swelling resulting from absorption can lead to bursting of the ion exchange containment column.

Ion exchange resins or fibers also have been disclosed for use in absorbent personal care devices (e.g., diapers) to control the pH of fluids that reach the skin, as set forth in Berg et al., U.S. Patent No. 4,685,909. The ion exchange resin is used in this application to reduce diaper rash, but the ion exchange resin is not significantly water absorbent and, therefore, does not improve the absorption and retention properties of the diaper.

Ion exchange resins having a composite particle containing acid and base ion exchange particles embedded together in a matrix resin, or having acid and base ion exchange particles adjacent to one another in a particle that is free of a matrix resin are disclosed in B.A. Bolto et al., *J. Polymer Sci.:Symposium No. 55*, John Wiley and Sons, Inc. (1976), pages 87-94. The Bolto et al. publication is directed to improving the reaction rates of ion exchange resins for water purification and does not utilize resins that absorb substantial amounts of water.

Other investigators have attempted to counteract the salt poisoning effect and thereby improve the performance of SAPs with respect to absorbing electrolyte-containing liquids, such as menses and urine. For example, Tanaka et al. U.S. Patent No. 5,274,018 discloses an SAP composition comprising a swellable hydrophilic polymer, such as polyacrylic acid, and an amount of an ionizable surfactant sufficient to form at least a monolayer

of surfactant on the polymer. In another embodiment, a cationic gel, such as a gel containing quaternized ammonium groups and in the hydroxide (i.e., OH) form, is admixed with an anionic gel (i.e., a polyacrylic acid) to remove electrolytes from the solution by ion exchange. Quaternized ammonium groups in the hydroxide form are very difficult and time-consuming to manufacture, thereby limiting the practical use of such cationic gels.

Wong U.S. Patent No. 4,818,598 discloses the addition of a fibrous anion exchange material, such as DEAE (diethylaminoethyl) cellulose, to a hydrogel, such as a polyacrylate, to improve absorption properties. The ion exchange resin "pretreats" the saline solution (e.g., urine) as the solution flows through an absorbent structure (e.g., a diaper). This pretreatment removes a portion of the salt from the saline. The conventional SAP present in the absorbent structure then absorbs the treated saline more efficiently than untreated saline. The ion exchange resin, *per se*, does not absorb the saline solution, but merely helps overcome the "salt poisoning" effect.

WO 96/17681 discloses admixing discrete anionic SAP particles, such as polyacrylic acid, with discrete polysaccharide-based cationic SAP particles to overcome the salt poisoning effect. Similarly, WO 96/15163 discloses combining a cationic SAP having at least 20% of the functional groups in a basic (i.e., OH) form with a cationic exchange resin, i.e., a nonswelling ion exchange resin, having at least 50% of the functional groups

in the acid form. WO 96/15180 discloses an absorbent material comprising an anionic SAP, e.g., a polyacrylic acid and an anion exchange resin, i.e., a nonswelling ion exchange resin.

5               These references disclose combinations that attempt to overcome the salt poisoning effect. However, the references merely teach the admixture of two types of particles, and do not suggest a single particle containing at least one microdomain  
10 of an acidic resin in contact, or in close proximity, with at least one microdomain of a basic resin. These references also do not teach a mixture of resin particles wherein one component of the mixture is particles of a multicomponent SAP.

15               It would be desirable to provide discrete SAP particles that exhibit exceptional water absorption and retention properties, especially with respect to electrolyte-containing liquids, and thereby overcome the salt poisoning effect. In  
20 addition, it would be desirable to provide discrete SAP particles that have an ability to absorb liquids quickly, demonstrate good fluid permeability and conductivity into and through the SAP particle, and have a high gel strength such that the hydrogel  
25 formed from the SAP particles does not deform or flow under an applied stress or pressure, when used alone or in a mixture with other water-absorbing resins.

SUMMARY OF THE INVENTION

5 The present invention is directed to multicomponent SAPs comprising at least one acidic water-absorbing resin, such as a polyacrylic acid, and at least one basic water-absorbing resin, such as poly(vinylamine), a polyethyleneimine, or a poly-(dialkylaminoalkyl acrylamide) or a poly(dialkyl- aminoalkyl methacrylamide), hereafter collectively referred to as poly(dialkylaminoalkyl(meth)acryl- amides).

10 More particularly, the present invention is directed to multicomponent SAP particles contain- ing at least one discrete microdomain of at least one acidic water-absorbing resin in contact with, or in close proximity to, at least one microdomain of at least one basic water-absorbing resin. The multicomponent SAP particles can contain a plurality of microdomains of the acidic water-absorbing resin and/or the basic water-absorbing resin dispersed throughout the particle. The acidic resin can be a strong or a weak acidic resin. Similarly, the basic resin can be a strong or a weak basic resin. A pre-ferred SAP contains one or more microdomains of at least one weak acidic resin and one or more microdo- mains of at least one weak basic resin. The proper- ties demonstrated by such preferred multicomponent SAP particles are unexpected because, in ion ex- change applications, the combination of a weak acid and a weak base is the least effective of any combination of a strong or weak acid ion exchange

resin with a strong or weak basic ion exchange resin.

Accordingly, one aspect of the present invention is to provide SAP particles that have a high absorption rate, have good permeability and gel strength, overcome the salt poisoning effect, and demonstrate an improved ability to absorb and retain electrolyte-containing liquids, such as saline, blood, urine, and menses. The present SAP particles contain discrete microdomains of acidic and basic resin, and during hydration, the particles resist coalescence but remain fluid permeable.

Another aspect of the present invention is to provide an SAP having improved absorption and retention properties compared to a conventional SAP, such as sodium polyacrylate. The present multi-component SAP particles are produced by any method that positions a microdomain of an acidic water-absorbing resin in contact with, or in close proximity to, a microdomain of a basic water-absorbing resin to provide a discrete particle. In one embodiment, the SAP particles are produced by coextruding an acidic water-absorbing hydrogel and a basic water-absorbing hydrogel to provide multicomponent SAP particles having a plurality of discrete microdomains of an acidic resin and a basic resin dispersed throughout the particle. Such SAP particles demonstrate improved absorption and retention properties, and permeability through and between particles compared to SAP compositions comprising a simple admixture of acidic resin particles and basic resin particles.

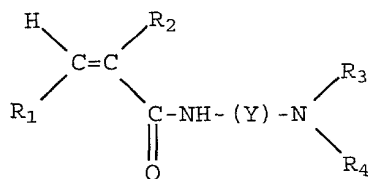
In another embodiment, the present multi-  
component SAP particles can be prepared by admixing  
dry particles of a basic resin with a hydrogel of an  
acidic resin, then extruding the resulting mixture  
5 to form multicomponent SAP particles having microdo-  
mains of a basic resin dispersed throughout a con-  
tinuous phase of an acidic resin. Alternatively,  
dry acidic resin particles can be admixed with a  
basic resin hydrogel, followed by extruding the re-  
10 sulting mixture to form multicomponent SAP particles  
having microdomains of an acidic resin dispersed in  
a continuous phase of a basic resin.

In addition, a multicomponent SAP particle  
containing microdomains of an acidic resin and a  
15 basic resin dispersed in a continuous phase of a  
matrix resin can be prepared by adding dry particles  
of the acidic resin and dry particles of the basic  
resin to a hydrogel of the matrix hydrogel, then  
extruding. Other forms of the present multicompo-  
20 nent SAP particles, such as agglomerated particles,  
interpenetrating polymer network forms, laminar  
forms, and concentric sphere forms, also demonstrate  
improved fluid absorption and retention properties.

In accordance with yet another important  
25 aspect of the present invention, the acidic and  
basic resins are lightly crosslinked, such as with a  
suitable polyfunctional vinyl polymer. In preferred  
embodiments, the acidic resin, the basic resin,  
and/or the entire multicomponent SAP particle are  
30 surface treated or annealed to further improve water  
absorption and retention properties, especially  
under a load.

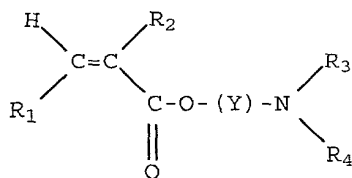
Yet another important feature of the present invention is to provide an SAP particle containing at least one microdomain of a weak acidic water-absorbing resin in contact with at least one microdomain of a weak basic water-absorbing resin.

An example of a weak acid resin is polyacrylic acid having 0% to 50% neutralized carboxylic acid groups (i.e., DN=0 to DN=50). Examples of weak basic water-absorbing resins are a poly(vinylamine), a polyethylenimine, and a poly(dialkylaminoalkyl (meth)acrylamide) prepared from a monomer either having the general structure formula (I)



(I)

or the ester analog of (I) having the general structure formula (II)



(II)

wherein  $R_1$  and  $R_2$ , independently, are selected from the group consisting of hydrogen and methyl, Y is a divalent straight chain or branched organic radical having 1 to 8 carbon atoms, and  $R_3$  and  $R_4$ , independently, are alkyl radicals having 1 to 4 carbon atoms. Examples of a strong basic water-absorbing resin are poly(vinylguanidine) and poly(allylguanidine).

Yet another aspect of the present invention is to provide an improved SAP material comprising a combination containing (a) multicomponent SAP particles, and (b) particles of a second water-absorbing resin selected from the group consisting of an acidic water-absorbing resin, a basic water-absorbing resin, and a mixture thereof. The combination contains about 10% to about 90%, by weight, multicomponent SAP particles and about 10% to about 90%, by weight, particles of the second water-absorbing resin.

Still another aspect of the present invention is to provide diapers having a core comprising multicomponent SAP particles or an SAP material of the present invention.

These and other aspects and advantages of the present invention will become apparent from the following detailed description of the preferred embodiments.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of a water-absorbing particle containing microdomains of a

first resin dispersed in a continuous phase of a second resin;

FIG. 2 is a schematic diagram of a water-absorbing particle containing microdomains of a first resin and microdomains of a second resin dispersed throughout the particle;

FIGS. 3A and 3B are schematic diagrams of a water-absorbing particle having a core microdomain of a first resin surrounded by a layer of a second resin;

FIGS. 4A-D are schematic diagrams of water-absorbing particles having a microdomain of a first resin in contact with a microdomain of a second resin;

FIGS. 5A and 5B are schematic diagrams of a water-absorbing particle having an interpenetrating network of a first resin and a second resin;

FIG. 6 contains plots of absorbance (in grams of synthetic urine per gram of multicomponent SAP particles) vs. annealing temperature for a one-hour annealing step;

FIG. 7 contains a plot of absorbance (in grams of synthetic urine per gram of multicomponent SAP particles) vs. time for an annealing step performed at 125°C;

FIGS. 8 and 9 contain plots of PUP at 0.7 psi (in g/g) vs. time (hrs) for present multicomponent SAP particles and prior art SAPs;

FIGS. 10 and 11 contain plots for initial Performance Under Pressure (PUP) capacity vs.  $t^{\frac{1}{2}}$  for present multicomponent SAP particles and prior art SAPs;

FIG. 12 contains plots of absorbance (in g/g) vs. weight percent of poly(AA) (DN=70) in a blend of multicomponent SAP particles and particles of poly(AA) (DN=70);

5           FIG. 13 contains plots of absorbance (in g/g) vs. weight percent of poly(AA) (DN=70) in a blend of particles of poly(AA) (DN=70), particles of poly(AA) (DN=0), and particles of poly(vinylamine);

10           FIGS. 14-17 are plots of absorbance (in g/g) vs. time (minutes) for a variety of blends of superabsorbent particles;

15           FIG. 18 is a plot of PUP at 0.7 psi vs. time (hrs) for a superabsorbent material containing 25% multicomponent SAP particles and 75% poly(AA) - (DN=70), by weight;

            FIG. 19 is a plot of initial PUP capacity vs.  $t^{1/2}$  for a superabsorbent material containing 25% multicomponent SAP particles and 75% poly(AA) - (DN=70), by weight;

20           FIGS. 20, 21, 23-26, and 28 are plots of acquisition time (seconds) vs. number of insults for a series of laboratory prepared diaper cores under a load of 0.7 psi; and

25           FIGS. 22, 27, and 29 are plots of acquisition rate vs. number of insults for a series of laboratory prepared diaper cores under a load of 0.7 psi.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to multicomponent SAP particles containing at least one microdomain of an acidic water-absorbing resin in close proximity to, and preferably in contact with, at least one microdomain of a basic water-absorbing resin. Each particle contains one or more microdomains of an acidic resin and one or more microdomains of a basic resin. The microdomains can be distributed nonhomogeneously or homogeneously throughout each particle.

Each multicomponent SAP particle of the present invention contains at least one acidic water-absorbing resin and at least one basic water-absorbing resin. In one embodiment, the SAP particles consist essentially of acidic resins and basic resins, and contain microdomains of the acidic and/or basic resins. In another embodiment, microdomains of the acidic and basic resins are dispersed in an absorbent matrix resin.

The multicomponent SAP particles of the present invention are not limited to a particular structure or shape. However, it is important that substantially each SAP particle contain at least one microdomain of an acidic water-absorbing resin and at least one microdomain of a basic water-absorbing resin in close proximity to one another. Improved water absorption and retention, and improved fluid permeability through and between SAP particles, are observed as long as the acidic resin microdomain and the basic resin microdomain are in close proximity

within the particle. In a preferred embodiment, the microdomains of acidic and basic resin are in contact.

In some embodiments, an idealized multi-  
5 component SAP particle of the present invention is analogous to a liquid emulsion wherein small droplets of a first liquid, i.e., the dispersed phase, are dispersed in a second liquid, i.e., the continuous phase. The first and second liquids are  
10 immiscible, and the first liquid, therefore, is homogeneously dispersed in the second liquid. The first liquid can be water or oil based, and conversely, the second liquid is oil or water based, respectively.

Therefore, in one embodiment, the multi-  
15 component SAP particles of the present invention can be envisioned as one or more microdomains of an acidic resin dispersed in a continuous phase of a basic resin, or as one or more microdomains of a  
20 basic resin dispersed in a continuous acid resin. These idealized multicomponent SAP particles are illustrated in FIG. 1 showing an SAP particle 10 having discrete microdomains 14 of a dispersed resin in a continuous phase of a second resin 12. If  
25 microdomains 14 comprise an acidic resin, then continuous phase 12 comprises a basic resin. Conversely, if microdomains 14 comprise a basic resin, then continuous phase 12 is an acidic resin.

In another embodiment, the SAP particles  
30 are envisioned as microdomains of an acidic resin and microdomains of a basic resin dispersed throughout each particle, without a continuous phase. This

embodiment is illustrated in FIG. 2, showing an idealized multicomponent SAP particle 20 having a plurality of microdomains of an acidic resin 22 and a plurality of microdomains of a basic resin 24 dispersed throughout particle 20.

In yet another embodiment, microdomains of the acidic and basic resins are dispersed throughout a continuous phase comprising a matrix resin. This embodiment also is illustrated in FIG. 1 wherein multicomponent SAP particle 10 contains one or more microdomains 14, each an acidic resin or a basic resin, dispersed in a continuous phase 12 of a matrix resin.

It should be understood that the microdomains within each particle can be of regular or irregular shape, and that the microdomains can be dispersed homogeneously or nonhomogeneously throughout each particle. Accordingly, another embodiment of the SAP particles is illustrated in FIG. 3A, showing an idealized multicomponent particle 30 having a core 32 of an acidic water-absorbing resin surrounded by a shell 34 of a basic water-absorbing resin. Conversely, core 32 can comprise a basic resin, and shell 34 can comprise an acidic resin.

FIG. 3B illustrates a similar embodiment having a core and concentric shells that alternate between shells of acidic resin and basic resin. In one embodiment, core 42 and shell 46 comprise an acidic water-absorbing resin, and shell 44 comprises a basic water-absorbing resin. Other embodiments include: core 42 and shell 46 comprising a basic

resin and shell 44 comprising an acidic resin, or  
core 42 comprising a matrix resin and shells 44 and  
46 comprising an acidic resin and a basic resin in  
alternating shells. Other configurations are  
5 apparent to persons skilled in the art, such as  
increasing the number of shells around the core.

FIGS. 4A and 4B illustrate embodiments of  
the present SAP particles wherein one microdomain of  
an acidic water-absorbing resin (i.e., 52 or 62) is  
10 in contact with one microdomain of a basic water-ab-  
sorbing resin (i.e., 54 or 64) to provide a multi-  
component SAP particle (i.e., 50 or 60). In these  
embodiments, the microdomains are dispersed nonhomo-  
geneously throughout the particle. The embodiments  
15 illustrated in FIG. 4 extend to SAP particles having  
more than one microdomain of each of the acidic  
resin and the basic resin, as illustrated in FIGS.  
4C and 4D, wherein multicomponent SAP particles 70  
and 80 contain alternating zones of acidic water-  
20 absorbing resin (e.g., 72 or 82) and basic water-  
absorbing resin (e.g., 74 or 84). Particles 70 and  
80 also can contain one or more layers 72, 74, 82,  
or 84 comprising a matrix resin.

In another embodiment, the multicomponent  
25 SAP particle comprises an interpenetrating polymer  
network (IPN), as illustrated in FIG. 5. An IPN is  
a material containing two polymers, each in network  
form. In an IPN, two polymers are synthesized  
and/or crosslinked in the presence of one another,  
30 and polymerization can be sequential or simultane-  
ous. Preparation of a sequential IPN begins with  
the synthesis of a first crosslinked polymer. Then,

monomers comprising a second polymer, a crosslinker, and initiator are swollen into the first polymer, and polymerized and crosslinked *in situ*. For example, a crosslinked poly(acrylic acid) network can  
5 be infused with solution containing a poly(vinyl-amine) and a crosslinker.

Simultaneous IPNs are prepared using a solution containing monomers of both polymers and their respective crosslinkers, which then are  
10 polymerized simultaneously by noninterfering modes, such as stepwise or chain polymerizations. A third method of synthesizing IPNs utilizes two lattices of linear polymers, mixing and coagulating the lat-  
tices, and crosslinking the two components simultane-  
15 ously. Persons skilled in the art are aware of other ways that an IPN can be prepared, each yielding a particular topology.

In most IPNs, the polymer phases separate to form distinct zones of the first polymer and  
20 distinct zones of the second polymer. In the remaining IPNs, the first and second polymers remain "soluble" in one another. Both forms of IPN have microdomains, and are multicomponent SAPs of the present invention.

25 FIGS. 5A and 5B illustrate IPN systems. FIG. 5A illustrates an IPN made by sequentially synthesizing the first and second polymers. FIG. 5B illustrates an IPN made by simultaneously polymeri-  
zing the first and second polymers. In FIGS. 5A and  
30 5B, the solid lines represent the first polymer (e.g., the acidic polymer) and the lightly dotted lines represent the second polymer (e.g., the basic

polymer). The heavy dots represent crosslinking sites.

In another embodiment, the multicomponent SAP particles are agglomerated particles prepared from fine particles of an acidic water-absorbing resin and fine particles of a basic water-absorbing resin. Typically, a fine resin particle has a diameter of less than about 200 microns ( $\mu$ ), such as about 0.01 to about 180  $\mu$ . The agglomerated multicomponent SAP particles are similar in structure to the particle depicted in FIG. 2. With respect to the agglomerated SAP particles, it is important that the particles have sufficient dry agglomeration (i.e., in the dry state) and wet agglomeration (i.e., in the hydrogel state) to retain single particle properties, i.e., the particles do not disintegrate into their constituent fine particles of acidic resin and basic resin.

In particular, the agglomerated particles have sufficient dry agglomeration to withstand fracturing. The dry agglomerated particles typically have an elastic character and, therefore, are not friable. The agglomerated particles also have sufficient wet strength to exhibit a property termed "wet agglomeration." Wet agglomeration is defined as the ability of an agglomerated multicomponent SAP particle to retain its single particle nature upon hydration, i.e., a lack of deagglomeration upon hydration. Wet agglomeration is determined by positioning fifty agglomerated SAP particles on a watch glass and hydrating the particles with 20 times their weight of a 1% (by weight) sodium

chloride solution (i.e., 1% saline). The particles are spaced sufficiently apart such that they do not contact one another after absorbing the saline and swelling. The SAP particles are allowed to absorb the saline solution for one hour, then the number of SAP particles is recounted under a microscope. The multicomponent SAP particles pass the wet agglomeration test if no more than about 53 hydrated particles are counted.

The multicomponent SAP particles of the present invention therefore comprise an acidic resin and a basic resin in a weight ratio of about 90:10 to about 10:90, and preferably about 20:80 to about 80:20. To achieve the full advantage of the present invention, the weight ratio of acidic resin to basic resin in a multicomponent SAP particle is about 30:70 to about 70:30. The acidic and basic resins can be distributed homogeneously or nonhomogeneously throughout the SAP particle.

The present multicomponent SAP particles contain at least about 50%, and preferably at least about 70%, by weight of acidic resin plus basic resin. To achieve the full advantage of the present invention, a multicomponent SAP particle contains about 80% to 100% by weight of the acidic resin plus basic resin. Components of the present SAP particles, other than the acidic and basic resin, typically, are matrix resins or other minor optional ingredients.

The multicomponent SAP particles of the present invention can be in any form, either regular or irregular, such as granules, fibers, beads,

powders, flakes, or foams, or any other desired shape, such as a sheet of the multicomponent SAP. In embodiments wherein the multicomponent SAP is prepared using an extrusion step, the shape of the SAP is determined by the shape of the extrusion die. The shape of the multicomponent SAP particles also can be determined by other physical operations, such as milling or by the method of preparing the particles, such as agglomeration.

In one preferred embodiment, the present SAP particles are in the form of a granule or a bead, having a particle size of about 10 to about 10,000 microns ( $\mu\text{m}$ ), and preferably about 100 to about 1,000  $\mu\text{m}$ . To achieve the full advantage of the present invention, the multicomponent SAP particles have a particle size of about 150 to about 800  $\mu\text{m}$ .

A microdomain is defined as a volume of an acidic resin or a basic resin that is present in a multicomponent SAP particle. Because each multicomponent SAP particle contains at least one microdomain of an acidic resin, and at least one microdomain of a basic resin, a microdomain has a volume that is less than the volume of the multicomponent SAP particle. A microdomain, therefore, can be as large as about 90% of the volume of multicomponent SAP particles.

Typically, a microdomain has a diameter of about 750  $\mu\text{m}$  or less, and preferably about 100  $\mu\text{m}$  or less. To achieve the full advantage of the present invention, a microdomain has a diameter of about 20  $\mu\text{m}$  or less. The multicomponent SAP particles also

40053660

contain microdomains that have submicron diameters, e.g., microdomain diameters of less than 1  $\mu\text{m}$ , preferably less than 0.1  $\mu\text{m}$ , to about 0.01  $\mu\text{m}$ .

In another preferred embodiment, the  
5 multicomponent SAP particles are in the shape of a fiber, i.e., an elongated, acicular SAP particle. The fiber can be in the shape of a cylinder, for example, having a minor dimension (i.e., diameter) and a major dimension (i.e., length). The fiber  
10 also can be in the form of a long filament that can be woven. Such filament-like fibers have a weight of below about 80 decitex, and preferably below about 70 decitex, per filament, for example, about 2 to about 60 decitex per filament. Tex is the weight  
15 in grams per one kilometer of fiber. One tex equals 10 decitex. For comparison, poly(acrylic acid) is about 4 decitex, and poly(vinylamine) is about 80 decitex.

Cylindrical multicomponent SAP fibers have  
20 a minor dimension (i.e., diameter of the fiber) less than about 1 mm, usually less than about 500  $\mu\text{m}$ , and preferably less than 250  $\mu\text{m}$ , down to about 50  $\mu\text{m}$ . The cylindrical SAP fibers can have a relatively short major dimension, for example, about 1 mm,  
25 e.g., in a fibrid, lamella, or flake-shaped article, but generally the fiber has a length of about 3 to about 100 mm. The filament-like fibers have a ratio of major dimension to minor dimension of at least 500 to 1, and preferably at least 1000 to 1, for  
30 example, up to and greater than 10,000 to 1.

Each multicomponent SAP particle contains one or more microdomains of an acidic water-absorb-

ing resin and one or more microdomains of a basic water-absorbing resin, either in contact or in close proximity to one another. As illustrated hereafter, the microdomain structure of the present SAP particles provides improved fluid absorption (both in amount of fluid absorbed and retained, and rate of absorption) compared to an SAP comprising a simple mixture of discrete acidic SAP resin particles and discrete basic SAP resin particles. In accordance with another important feature of the present invention, the present multicomponent SAP particles also demonstrated improved permeability, both through an individual particle and between particles. The present SAP particles, therefore, have an improved ability to rapidly absorb a fluid, even in "gush" situations, for example, when used in diapers to absorb urine.

The features of good permeability, absorption and retention properties, especially of electrolyte-containing liquids, demonstrated by the present multicomponent SAP particles, is important with respect to practical uses of an SAP. These improved properties are attributed, in part, to the fact that electrolyte removal from the liquid is facilitated by contacting a single particle (which, in effect, performs an essentially simultaneous deionization of the liquid), as opposed to the liquid having to contact individual acidic and basic particles (which, in effect, performs a sequential two-step deionization).

If a blend of acidic resin particles and basic resin particles is used, the particles typ-

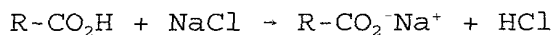
ically have a small particle size. A small particle size is required to obtain desirable desalination kinetics, because the electrolyte is removed in a stepwise manner, with the acidic resin removing the cation and the basic resin removing the anion. The electrolyte-containing fluid, therefore, must contact two particles for desalination, and this process is facilitated by small particle sized SAPs. Small particles, however, have the effect of reducing flow of the fluid through and between SAP particles, i.e., permeability is reduced and a longer time is required to absorb the fluid.

In addition, in practical use, such as in diapers, SAPs are used in conjunction with a cellulosic pulp. If a blend of acidic resin particles and basic resin particles is used as the SAP, the cellulosic pulp can cause a separation between the acidic resin particles and basic resin particles, which adversely affects desalination. The present multidomain composites overcome this problem because the acidic resin and basic resin are present in a single particle. The introduction of cellulosic pulp, therefore, cannot separate the acidic and basic resin and cannot adversely affect desalination by the SAP.

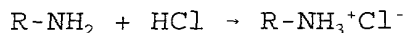
A single multicomponent SAP particle simultaneously desalinates an electrolyte-containing liquid. Desalination is essentially independent of particle size. Accordingly, the present multicomponent SAP particles can be of a larger size. These features allow for improved liquid permeability through and between the SAP particles, and re-

sults in a more rapid absorption of the electrolyte-containing liquid.

The following schematic reactions illustrate the reactions which occur to deionize, e.g., desalinate, an aqueous saline solution, and that are performed essentially simultaneously in a single microcomposite SAP particle, but are performed stepwise in a simple mixture of acidic and basic resins:



(acidic resin)



(basic resin).

The present multicomponent SAP particle, can be in a form wherein a microdomain of an acidic water-absorbing resin is in contact with a microdomain of a basic water-absorbing resin. In another embodiment, the SAP particles can be in a form wherein at least one microdomain of an acidic water-absorbing resin is dispersed in a continuous phase of a basic water-absorbing resin. Alternatively, the multicomponent SAP can be in a form wherein at least one microdomain of a basic resin is dispersed in a continuous phase of an acidic resin. In another embodiment, at least one microdomain of one or more acidic resin and at least one microdomain of one or more basic resin comprise the entire SAP particle, and neither type of resin is considered the dispersed or the continuous phase. In yet another embodiment, at least one microdomain of an acidic resin and at least one microdomain of a basic resin are dispersed in a matrix resin.

4005660

An acidic water-absorbing resin present in a multicomponent SAP particle can be either a strong or a weak acidic water-absorbing resin. The acidic water-absorbing resin can be a single resin, or a mixture of resins. The acidic resin can be a homopolymer or a copolymer. The identity of the acidic water-absorbing resin is not limited as long as the resin is capable of swelling and absorbing at least ten times its weight in water, when in a neutralized form. The acidic resin is present in its acidic form, i.e., about 50% to 100% of the acidic moieties are present in the free acid form. As illustrated hereafter, although the free acid form of a acidic water-absorbing resin is generally a poor water absorbent, the combination of an acidic resin and a basic resin in a present multicomponent SAP particle provides excellent water absorption and retention properties.

The acidic water-absorbing resin typically is a lightly crosslinked acrylic-type resin, such as lightly crosslinked polyacrylic acid. The lightly crosslinked acidic resin typically is prepared by polymerizing an acidic monomer containing an acyl moiety, e.g., acrylic acid, or a moiety capable of providing an acid group, i.e., acrylonitrile, in the presence of a crosslinker, i.e., a polyfunctional organic compound. The acidic resin can contain other copolymerizable units, i.e., other monoethylenically unsaturated comonomers, well known in the art, as long as the polymer is substantially, i.e., at least 10%, and preferably at least 25%, acidic monomer units. To achieve the full advantage of the

present invention, the acidic resin contains at least 50%, and more preferably, at least 75%, and up to 100%, acidic monomer units. The other copolymerizable units can, for example, help improve the hydrophilicity of the polymer.

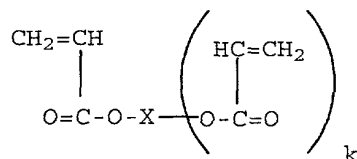
Ethylenically unsaturated carboxylic acid and carboxylic acid anhydride monomers useful in the acidic water-absorbing resin include acrylic acid, methacrylic acid, ethacrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -cyanoacrylic acid,  $\beta$ -methylacrylic acid (crotonic acid),  $\alpha$ -phenylacrylic acid,  $\beta$ -acryloxypropionic acid, sorbic acid,  $\alpha$ -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid,  $\beta$ -stearylacrylic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene, and maleic anhydride.

Ethylenically unsaturated sulfonic acid monomers include aliphatic or aromatic vinyl sulfonic acids, such as vinylsulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, acrylic and methacrylic sulfonic acids, such as sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid, and 2-acrylamide-2-methylpropane sulfonic acid.

As set forth above, polymerization of acidic monomers, and copolymerizable monomers, if present, most commonly is performed by free radical processes in the presence of a polyfunctional organic compound. The acidic resins are crosslinked

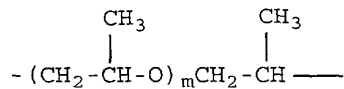
to a sufficient extent such that the polymer is water insoluble. Crosslinking renders the acidic resins substantially water insoluble, and, in part, serves to determine the absorption capacity of the resins. For use in absorption applications, an acidic resin is lightly crosslinked, i.e., has a crosslinking density of less than about 20%, preferably less than about 10%, and most preferably about 0.01% to about 7%.

A crosslinking agent most preferably is used in an amount of less than about 7 wt%, and typically about 0.1 wt% to about 5 wt%, based on the total weight of monomers. Examples of crosslinking polyvinyl monomers include, but are not limited to, polyacrylic (or polymethacrylic) acid esters represented by the following formula (III); and bisacrylamides, represented by the following formula (IV),

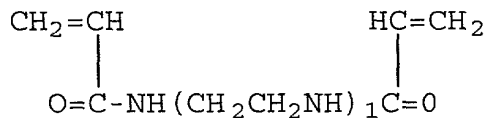


(III)

wherein x is ethylene, propylene, trimethylene, cyclohexyl, hexamethylene, 2-hydroxypropylene,  $-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2-$ , or



n and m are each an integer 5 to 40, and k is 1 or 2;



(IV)

wherein 1 is 2 or 3.

The compounds of formula (III) are prepared by reacting polyols, such as ethylene glycol, propylene glycol, trimethylolpropane, 1,6-hexanediol, glycerin, pentaerythritol, polyethylene glycol, or polypropylene glycol, with acrylic acid or methacrylic acid. The compounds of formula (IV) are obtained by reacting polyalkylene polyamines, such as diethylenetriamine and triethylenetetramine, with acrylic acid.

Specific crosslinking monomers include, but are not limited to, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, ethylene

glycol dimethacrylate, 1,6-hexanediol diacrylate,  
1,6-hexanediol dimethacrylate, neopentyl glycol  
dimethacrylate, polyethylene glycol diacrylate,  
polyethylene glycol dimethacrylate, triethylene  
5 glycol diacrylate, triethylene glycol dimethacryl-  
ate, tripropylene glycol diacrylate, tetraethylene  
glycol diacrylate, tetraethylene glycol dimethacryl-  
ate, dipentaerythritol pentaacrylate, pentaeryth-  
ritol tetraacrylate, pentaerythritol triacrylate,  
10 trimethylolpropane triacrylate, trimethylolpropane  
trimethacrylate, tris(2-hydroxyethyl)isocyanurate  
triacrylate, tris(2-hydroxyethyl)isocyanurate tri-  
methacrylate, divinyl esters of a polycarboxylic  
acid, diallyl esters of a polycarboxylic acid,  
15 triallyl terephthalate, diallyl maleate, diallyl  
fumarate, hexamethylenebismaleimide, trivinyl tri-  
mellitate, divinyl adipate, diallyl succinate, a  
divinyl ether of ethylene glycol, cyclopentadiene  
diacrylate, tetraallyl ammonium halides, or mixtures  
20 thereof. Compounds such as divinylbenzene and di-  
vinyl ether also can be used to crosslink the poly-  
(dialkylaminoalkyl acrylamides). Especially pre-  
ferred crosslinking agents are N,N'-methylenebis-  
acrylamide, N,N'-methylenebismethacrylamide, ethyl-  
25 ene glycol dimethacrylate, and trimethylolpropane  
triacrylate.

The acidic resin, either strongly acidic  
or weakly acidic, can be any resin that acts as an  
SAP in its neutralized form. The acidic resins  
30 typically contain a plurality of carboxylic acid,  
sulfonic acid, phosphonic acid, phosphoric acid,  
and/or sulfuric acid moieties. Examples of acidic

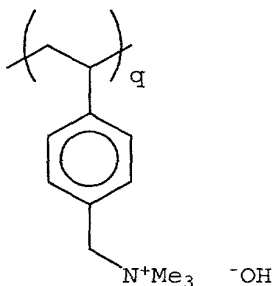
resins include, but are not limited to, polyacrylic acid, hydrolyzed starch-acrylonitrile graft copolymers, starch-acrylic acid graft copolymers, saponified vinyl acetate-acrylic ester copolymers, 5 hydrolyzed acrylonitrile copolymers, hydrolyzed acrylamide copolymers, ethylene-maleic anhydride copolymers, isobutylene-maleic anhydride copolymers, poly(vinylsulfonic acid), poly(vinylphosphonic acid), poly(vinylphosphoric acid), poly(vinylsulfuric acid), 10 sulfonated polystyrene, poly(aspartic acid), poly(lactic acid), and mixtures thereof. The preferred acidic resins are the polyacrylic acids.

The multicomponent SAPs can contain individual microdomains that: (a) contain a single 15 acidic resin or (b) contain more than one, i.e., a mixture, of acidic resins. The multicomponent SAPs also can contain microdomains wherein, for the acidic component, a portion of the acidic microdomains comprise a first acidic resin or acidic 20 resin mixture, and the remaining portion comprises a second acidic resin or acidic resin mixture.

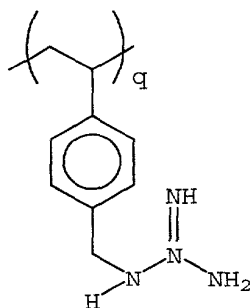
Analogous to the acidic resin, the basic water-absorbing resin in the present SAP particles can be a strong or weak basic water-absorbing 25 resins. The basic water-absorbing resin can be a single resin or a mixture of resins. The basic resin can be a homopolymer or a copolymer. The identity of the basic resin is not limited as long as the basic resin is capable of swelling and absorbing at least 10 times its weight in water, when 30 in a charged form. The weak basic resin typically is present in its free base, or neutral, form, i.e.,

about 50% to about 100% of the basic moieties, e.g., amino groups, are present in a neutral, uncharged form. The strong basic resins typically are present in the hydroxide (OH) or bicarbonate (HCO<sub>3</sub>) form.

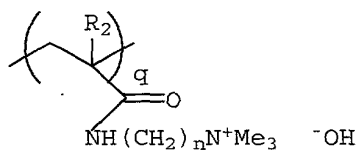
- 5           The basic water-absorbing resin typically is a lightly crosslinked acrylic type resin, such as a poly(vinylamine) or a poly(dialkylaminoalkyl (meth)acrylamide). The basic resin also can be a polymer such as a lightly crosslinked polyethylen-
- 10   imine, a poly(allylamine), a poly(allylguanidine), a poly(dimethyldiallylammonium hydroxide), a quaternized polystyrene derivative, such as



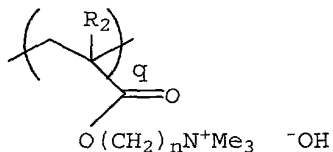
a guanidine-modified polystyrene, such as



a quaternized poly((meth)acrylamide) or ester analog, such as



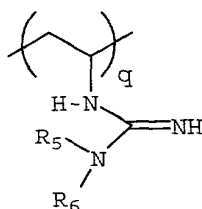
or



5

wherein Me is methyl,  $R_2$  is hydrogen or methyl,  $n$  is a number 1 to 8, and  $q$  is a number from 10 to about 100,000, or a poly(vinylguanidine), i.e., poly(VG), a strong basic water-absorbing resin having the

10 general structural formula (V)



(V)

wherein  $q$  is a number from 10 to about 100,000, and  $R_5$  and  $R_6$ , independently, are selected from the group consisting of hydrogen,  $C_1$ - $C_4$  alkyl,  $C_3$ - $C_6$  cycloalkyl, benzyl, phenyl, alkyl-substituted phenyl, naphthyl, and similar aliphatic and aromatic groups. The lightly crosslinked basic water-absorbing resin can contain other copolymerizable units and is cross-linked using a polyfunctional organic compound, as set forth above with respect to the acidic water-absorbing resin.

A basic water-absorbing resin used in the present SAP particles typically contains an amino or a guanidino group. Accordingly, a water-soluble basic resin also can be crosslinked in solution by suspending or dissolving an uncrosslinked basic resin in an aqueous or alcoholic medium, then adding a di- or polyfunctional compound capable of crosslinking the basic resin by reaction with the amino groups of the basic resin. Such crosslinking agents include, for example, multifunctional aldehydes (e.g., glutaraldehyde), multifunctional acrylates (e.g., butanediol diacrylate, TMPTA), halohydrins (e.g., epichlorohydrin), dihalides (e.g., dibromopropane), disulfonate esters (e.g.,  $ZA(O_2)O-(CH_2)_n-$

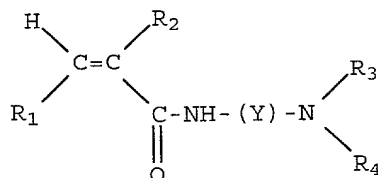
OS(O)<sub>2</sub>Z, wherein n is 1 to 10, and Z is methyl or  
tosyl), multifunctional epoxies (e.g., ethylene  
glycol diglycidyl ether), multifunctional esters  
(e.g., dimethyl adipate), multifunctional acid  
5 halides (e.g., oxalyl chloride), multifunctional  
carboxylic acids (e.g., succinic acid), carboxylic  
acid anhydrides (e.g., succinic anhydride), organic  
titanates (e.g., TYZOR AA from DuPont), melamine  
resins (e.g., CYMEL 301, CYMEL 303, CYMEL 370, and  
10 CYMEL 373 from Cytec Industries, Wayne, NJ),  
hydroxymethyl ureas (e.g., N,N'-dihydroxymethyl-4,5-  
dihydroxyethyleneurea), and multifunctional isocya-  
nates (e.g., toluene diisocyanate or methylene  
diisocyanate). Crosslinking agents also are dis-  
15 closed in Pinschmidt, Jr. et al. U.S. Patent No.  
5,085,787, incorporated herein by reference, and in  
EP 450 923.

Conventionally, the crosslinking agent is  
water or alcohol soluble, and possesses sufficient  
20 reactivity with the basic resin such that crosslink-  
ing occurs in a controlled fashion, preferably at a  
temperature of about 25°C to about 150°C. Preferred  
crosslinking agents are ethylene glycol diglycidyl  
ether (EGDGE), a water-soluble diglycidyl ether, and  
25 a dibromoalkane, an alcohol-soluble compound.

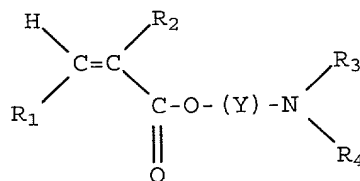
The basic resin, either strongly or weakly  
basic, therefore, can be any resin that acts as an  
SAP in its charged form. The basic resin typically  
contains amino or guanidino moieties. Examples of  
30 basic resins include a poly(vinylamine), a poly-  
ethylenimine, a poly(vinylguanidine), a poly(allyl-  
amine), a poly(allylguanidine), or a poly(dialkyl-

FOUO 4605660

aminoalkyl (meth)acrylamide) prepared by polymerizing and lightly crosslinking a monomer having the structure



or its ester analog



5

wherein  $R_1$  and  $R_2$ , independently, are selected from the group consisting of hydrogen and methyl, Y is a divalent straight chain or branched organic radical having 1 to 8 carbon atoms, and  $R_3$  and  $R_4$ , independently, are alkyl radicals having 1 to 4 carbon atoms. Preferred basic resins include a poly(vinylamine), polyethylenimine, poly(vinylguanadine), poly(dimethylaminoethyl acrylamide) (poly(DAEA)), and poly(dimethylaminopropyl methacrylamide) (poly(DMAPMA)). Analogous to microdomains of an acidic resin, the present multicomponent SAPs can contain microdomains of a single basic resin, microdomains

10

15

containing a mixture of basic resins, or microdomains of different basic resins.

5 The present multicomponent SAPs can be prepared by various methods. It should be understood that the exact method of preparing a multicomponent SAP is not limited by the following embodiments. Any method that provides a particle having at least one microdomain of an acidic resin in contact with or in close proximity to at least one microdomain of a basic resin is suitable.

10 In one method, dry particles of a basic resin, optionally surface crosslinked and/or annealed, are admixed into a rubbery gel of an acidic resin. The resulting mixture is extruded, then dried, and optionally surface crosslinked and/or annealed, to provide multicomponent SAP particles having microdomains of a basic resin dispersed in a continuous phase of an acidic resin. Alternatively, particles of an acidic resin, optionally surface crosslinked and/or annealed, can be admixed into a rubbery gel of a basic resin, and the resulting mixture is extruded and dried, and optionally surface crosslinked and/or annealed, to provide multicomponent SAP particles having microdomains of an acidic resin dispersed in a continuous phase of a basic resin.

25 In another method, dry particles of an acidic resin can be admixed with dry particles of a basic resin, and the resulting mixture is formed into a hydrogel, then extruded, to form multicomponent SAP particles.

In yet another method, a rubbery gel of an acidic resin and a rubbery gel of a basic resin, each optionally surface crosslinked and/or annealed, are coextruded, and the coextruded product is dried, and  
5 optionally surface crosslinked and/or annealed, to form multicomponent SAP particles containing microdomains of the acidic resin and the basic resin dispersed throughout the particle.

The method of preparing the present multi-  
10 component SAP particles, therefore, is not limited, and does not require an extrusion step. Persons skilled in the art are aware of other methods of preparation wherein the multicomponent SAP contains at least one microdomain of an acidic resin and at  
15 least one microdomain of a basic resin in contact or in close proximity with each other. One example is agglomeration of fine particles of at least one acidic resin and at least one basic resin with each other, and optionally a matrix resin, to provide a  
20 multicomponent SAP particle containing microdomains of an acidic and/or basic resin. The multicomponent SAP particles can be ground to a desired particle size, or can be prepared by techniques that yield the desired particle size. Other nonlimiting methods of  
25 preparing an SAP particle of the present invention are set forth in the examples.

In embodiments wherein an acidic resin and a basic resin are present as microdomains within a matrix of a matrix resin, particles of an acidic  
30 resin and a basic resin are admixed with a rubbery gel of a matrix resin, and the resulting mixture is extruded, then dried, to form multicomponent SAP

particles having microdomains of an acidic resin and a basic resin dispersed in a continuous phase of a matrix resin. Alternatively, rubbery gels of an acidic resin, basic resin, and matrix resin can be coextruded to provide a multicomponent SAP containing microdomains of an acidic resin, a basic resin, and a matrix resin dispersed throughout the particle. In this embodiment, the acidic resin, basic resin, and resulting multicomponent SAP, each can be optionally surface crosslinked and/or annealed.

The matrix resin is any resin that allows fluid transport such that a liquid medium can contact the acidic and basic resin. The matrix resin typically is a hydrophilic resin capable of absorbing water. Nonlimiting examples of matrix resins include poly(vinyl alcohol), poly(N-vinylformamide), polyethylene oxide, poly(meth)acrylamide, poly(hydroxyethyl acrylate), hydroxyethylcellulose, methylcellulose, and mixtures thereof. The matrix resin also can be a conventional water-absorbing resin, for example, a polyacrylic acid neutralized greater than 50 mole %, and typically greater than 70 mole %.

In preferred embodiments, the acidic resin, the basic resin, and/or the multicomponent SAP particles are surface treated and/or annealed. Surface treatment and/or annealing results in surface crosslinking of the particle. In especially preferred embodiments, the acidic and/or basic resins comprising the multicomponent SAP particles are surface treated and/or annealed, and the entire multicomponent SAP particle is surface treated and/or annealed. It has been found that surface treating and/or

annealing of an acidic resin, a basic resin, and/or a multicomponent SAP particle of the present invention enhances the ability of the resin or multicomponent SAP particle to absorb and retain aqueous media under  
5 a load.

Surface crosslinking is achieved by contacting an acidic resin, a basic resin, and/or a multicomponent SAP particle with a solution of a surface crosslinking agent to wet predominantly only  
10 the outer surfaces of the resin or SAP particle. Surface crosslinking and drying of the resin or multicomponent SAP particle then is performed, preferably by heating at least the wetted surfaces of the resin or multicomponent SAP particles.

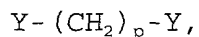
15 Typically, the resins and/or SAP particles are surface treated with a solution of a surface crosslinking agent. The solution contains about 0.01% to about 4%, by weight, surface crosslinking agent, and preferably about 0.4% to about 2%, by  
20 weight, surface crosslinking agent in a suitable solvent, for example, water or an alcohol. The solution can be applied as a fine spray onto the surface of freely tumbling resin particles or multicomponent SAP particles at a ratio of about 1:0.01 to  
25 about 1:0.5 parts by weight resin or SAP particles to solution of surface crosslinking agent. The surface crosslinker is present in an amount of 0% to about 5%, by weight of the resin or SAP particle, and preferably 0% to about 0.5% by weight. To achieve  
30 the full advantage of the present invention, the surface crosslinker is present in an amount of about 0.001% to about 0.1% by weight.

The crosslinking reaction and drying of the surface-treated resin or multicomponent SAP particles are achieved by heating the surface-treated polymer at a suitable temperature, e.g., about 25°C to about 150°C, and preferably about 105°C to about 120°C. However, any other method of reacting the crosslinking agent to achieve surface crosslinking of the resin or multicomponent SAP particles, and any other method of drying the resin or multicomponent SAP particles, such as microwave energy, or the such as, can be used.

With respect to the basic resin, or multicomponent SAP particles having a basic resin present on the exterior surface of the particles, suitable surface crosslinking agents include di- or polyfunctional molecules capable of reacting with amino groups and crosslinking a basic resin. Preferably, the surface crosslinking agent is alcohol or water soluble and possesses sufficient reactivity with a basic resin such that crosslinking occurs in a controlled fashion at a temperature of about 25°C to about 150°C.

Nonlimiting examples of suitable surface crosslinking agents for basic resins include:

(a) dihalides and disulfonate esters, for example, compounds of the formula



wherein p is a number from 2 to 12, and Y, independently, is halo (preferably bromo), tosylate, mesylate, or other alkyl or aryl sulfonate esters;

(b) multifunctional aziridines;

(c) multifunctional aldehydes, for example, glutaraldehyde, trioxane, paraformaldehyde, terephthaldehyde, malonaldehyde, and glyoxal, and acetals and bisulfites thereof;

5 (d) halohydrins, such as epichlorohydrin;

(e) multifunctional epoxy compounds, for example, ethylene glycol diglycidyl ether, bisphenol A diglycidyl ether, and bisphenol F diglycidyl ether,

10 (f) multifunctional carboxylic acids and esters, acid chlorides, and anhydrides derived therefrom, for example, di- and polycarboxylic acids containing 2 to 12 carbon atoms, and the methyl and ethyl esters, acid chlorides, and anhydrides derived therefrom, such as oxalic acid, adipic acid, succinic  
15 acid, dodecanoic acid, malonic acid, and glutaric acid, and esters, anhydrides, and acid chlorides derived therefrom;

(g) organic titanates, such as TYZOR AA, available from E.I. DuPont de Nemours, Wilmington,  
20 DE;

(h) melamine resins, such as the CYMEL resins available from Cytec Industries, Wayne, NJ;

(i) hydroxymethyl ureas, such as N,N'-dihydroxymethyl-4,5-dihydroxyethylene urea;

25 (j) multifunctional isocyanates, such as toluene diisocyanate, isophorone diisocyanate, methylene diisocyanate, xylene diisocyanate, and hexamethylene diisocyanate; and

(k) other crosslinking agents for basic  
30 water-absorbing resins known to persons skilled in the art.

100-403660

A preferred surface crosslinking agent is a dihaloalkane, ethylene glycol diglycidyl ether (EGDGE), or a mixture thereof, which crosslink a basic resin at a temperature of about 25°C to about 150°C. Especially preferred surface crosslinking agents are dibromoalkanes containing 3 to 10 carbon atoms and EGDGE.

With respect to the acidic water-absorbing resins, or multicomponent SAP particles having an acidic resin on the exterior surface of the particles, suitable surface crosslinking agents are capable of reacting with acid moieties and crosslinking the acidic resin. Preferably, the surface crosslinking agent is alcohol soluble or water soluble, and possesses sufficient reactivity with an acidic resin such that crosslinking occurs in a controlled fashion, preferably at a temperature of about 25°C to about 150°C.

Nonlimiting examples of suitable surface crosslinking agents for acidic resins include:

- (a) polyhydroxy compounds, such as glycols and glycerol;
- (b) metal salts;
- (c) quaternary ammonium compounds;
- (d) a multifunctional epoxy compound;
- (e) an alkylene carbonate, such as ethylene carbonate or propylene carbonate;
- (f) a polyaziridine, such as 2,2-bishydroxymethyl butanol tris[3-(1-aziridine propionate)];
- (g) a haloepoxy, such as epichlorhydrin;
- (h) a polyamine, such as ethylenediamine;

(i) a polyisocyanate, such as 2,4-toluene diisocyanate; and

(j) other crosslinking agents for acidic water-absorbing resins known to persons skilled in the art.

In addition to, or in lieu of, surface treating, the acidic resin, the basic resin, the matrix resin, or the entire SAP particle, or any combination thereof, can be annealed to improve water absorption and retention properties under a load. It has been found that heating a resin for a sufficient time at a sufficient temperature above the T<sub>g</sub> (glass transition temperature) of the resin or microdomains improves the absorption properties of the resin.

FIGS. 6 and 7 contain graphs showing the effect of annealing time and temperature on the absorption properties of a multicomponent SAP particle of the present invention comprising 55% by weight poly(vinylamine) and 45% by weight poly(acrylic acid), made by the method set forth hereafter in Example 12.

The graphs in FIGS. 6 and 7 show that heating an SAP particle of the present invention for about 20 to about 120 minutes at a temperature of about 60°C to about 150°C improves absorption properties. The absorption properties, i.e., AUL and AUNL, graphed in FIGS. 6 and 7 are discussed in detail hereafter. Preferably, annealing is performed for about 30 to about 100 minutes at about 80°C to about 140°C. To achieve the full advantage of annealing, the SAP particles are annealed for about 40 to about 90 minutes at about 100°C to about 140°C.

In accordance with an important feature of the present invention, a strong acidic resin can be used with either a strong basic resin or a weak basic resin, or a mixture thereof. A weak acidic resin can  
5 be used with a strong basic resin or a weak basic resin, or a mixture thereof. Preferably, the acidic resin is a weak acidic resin and the basic resin is a weak basic resin. This result is unexpected in view of the ion exchange art wherein a combination of a  
10 weak acidic resin and a weak basic resin does not perform as well as other combinations, e.g., a strong acidic resin and a strong basic resin. In more preferred embodiments, the weak acidic resin, the weak basic resin, and/or the multicomponent SAP particles  
15 are surface crosslinked and/or annealed.

As previously discussed, sodium poly(acrylate) conventionally is considered the best SAP, and, therefore, is the most widely used SAP in commercial applications. Sodium poly(acrylate) has polyelectro-  
20 lytic properties that are responsible for its superior performance in absorbent applications. These properties include a high charge density, and charge relatively close to the polymer backbone.

However, an acidic resin in the free acid  
25 form, or a basic resin in the free base form, typically do not function as a commercially useful SAP because there is no ionic charge on either type of polymer. A poly(acrylic acid) resin, or a poly-(vinylamine) resin, are neutral polymers, and,  
30 accordingly, do not possess the polyelectrolytic properties necessary to provide SAPs useful commercially in diapers, catamenial devices, and similar

102280-460560

absorbent articles. The driving force for water absorption and retention, therefore, is lacking. This is illustrated in Tables 1 and 2 showing the relatively poor absorption and retention properties  
5 for a neutral poly(DAEA) in absorbing synthetic urine. However, when converted to a salt, an acidic resin, such as a polyacrylic acid, or a basic resin, such as a poly(dialkylaminoalkyl (meth)acrylamide), then behave such as a commercially useful SAP.

10 It has been found that basic resins, in their free base form, are useful components in superabsorbent materials further containing an acidic water-absorbing resin. For example, a superabsorbent material comprising an admixture of a poly(dialkyl-  
15 aminoalkyl (meth)acrylamide) and an acidic water-absorbing resin, such as polyacrylic acid, demonstrates good water absorption and retention properties. Such an SAP material comprises two uncharged, slightly crosslinked polymers, each of which is  
20 capable of swelling and absorbing aqueous media. When contacted with water or an aqueous electrolyte-containing medium, the two uncharged polymers neutralize each other to form a superabsorbent material. This also reduces the electrolyte content  
25 of the medium absorbed by polymer, further enhancing the polyelectrolyte effect. Neither polymer in its uncharged form behaves as an SAP by itself when contacted with water. However, superabsorbent materials, which contain a simple mixture of two resins,  
30 one acidic and one basic, are capable of acting as an absorbent material because the two resins are converted to their polyelectrolyte form. These super-

702280 4605E660

absorbent materials have demonstrated good water absorption and retention properties. However, the present multicomponent SAP particles, containing at least one microdomain of an acidic resin and at least one microdomain of a basic resin, exhibit improved water absorption and retention, and improved permeability, over simple mixtures of acidic resin particles and basic resin particles.

In the present multicomponent SAP particles, the weak basic resin is present in its free base, e.g., amine, form, and the acidic resin is present in its free acid form. It is envisioned that a low percentage, i.e., about 50% or less, of the amine and/or acid functionalities can be in their charged form. The low percentage of charged functionalities does not adversely affect performance of the SAP particles, and can assist in the initial absorption of a liquid. A strong basic resin is present in the hydroxide or bicarbonate, i.e., charged, form.

The present multicomponent SAP particles are useful in articles designed to absorb large amounts of liquids, especially electrolyte-containing liquids, such as in diapers and catamenial devices.

The following nonlimiting examples illustrate the preparation of the multicomponent SAP particles of the present invention.

EXAMPLE 1

Preparation of Poly(acrylic acid)  
0% Neutralized (Poly(AA) DN=0)

5 A monomer mixture containing acrylic acid  
(270 grams), deionized water (810 grams), methylene-  
bisacrylamide (0.4 grams), sodium persulfate (0.547  
grams), and 2-hydroxy-2-methyl-1-phenyl-propan-1-one  
(0.157 grams) was prepared, then sparged with  
10 nitrogen for 15 minutes. The monomer mixture was  
placed into a shallow glass dish, then the monomer  
mixture was polymerized under 15 mW/cm<sup>2</sup> of UV light  
for 25 minutes. The resulting poly(AA) was a rubbery  
gel.

15 The rubbery poly(AA) gel was cut into small  
pieces, then extruded through a KitchenAid Model K5SS  
mixer with meat grinder attachment. The extruded gel  
was dried in a forced-air oven at 120°C, and finally  
ground and sized through sieves to obtain the desired  
particle size.

20 This procedure provided a lightly cross-  
linked polyacrylic acid hydrogel with a degree of  
neutralization of zero (DN=0).

EXAMPLE 2

Preparation of Poly(dimethylaminoethyl)  
acrylamide) (Poly (DAEA))

25 A monomer mixture containing 125 grams N-  
(2-dimethylaminoethyl) acrylamide (DAEA), 300 grams  
deionized water, 0.6 gram methylenebisacrylamide, and  
0.11 grams V-50 initiator (i.e., 2,2'-azobis(2-ami-

5 dinopropane)hydrochloride initiator available from  
Wako Pure Chemical Industries, Inc., Osaka, Japan)  
was sparged with argon for 15 minutes. Then the  
resulting reaction mixture was placed in a shallow  
10 dish and polymerized under 15 mW/cm<sup>2</sup> of UV light for  
25 minutes. The polymerization was exothermic,  
eventually reaching about 100°C. The resulting  
lightly crosslinked poly(DAEA) was a rubbery gel.  
The rubbery poly(DAEA) gel was crumbled by hand, then  
15 dried at 60°C for 16 hours, and finally ground and  
sized through sieves to obtain the desired particle  
size.

### EXAMPLE 3

#### Preparation of Poly(dimethylaminopropyl methacrylamide) (Poly(DMAPMA))

15 A monomer mixture containing DMAPMA monomer  
(100 grams), deionized water (150 grams), methylene-  
bisacrylamide (0.76 grams) and V-50 initiator (0.72  
grams) was placed in a glass beaker. The monomer  
20 mixture was purged with argon for 25 minutes,  
covered, and then placed in an oven at about 60°C for  
about 60 hours. The resulting lightly crosslinked  
poly(DMAPMA) was a rubbery gel. The rubbery poly-  
(DMAPMA) gel was crumbled by hand, dried at 60°C for  
25 16 hours, and then ground and sized through sieves to  
obtain the desired particle size.

EXAMPLE 4

Preparation of a Poly(N-vinylformamide)  
and a Poly(vinylamine)

5 A monomer mixture containing N-vinylform-  
amide (250 grams), deionized water (250 grams),  
methylenebisacrylamide (1.09) grams), and V-50  
initiator (0.42 grams) was placed in a shallow dish,  
then polymerized under an ultraviolet lamp as set  
forth in Example 1 until the mixture polymerized into  
10 a rubbery gel. The lightly crosslinked poly(N-vinyl-  
formamide) then was hydrolyzed with a sodium  
hydroxide solution to yield a lightly crosslinked  
poly(vinylamine).

EXAMPLE 5

15 Preparation of a Strong  
Acidic Water-Absorbing Resin

A monomer mixture containing acrylic acid  
(51 grams), 2-acrylamido-2-methyl-1-propanesulfonic  
acid (AMPS, 25.8 grams), deionized water (230 grams),  
20 methylenebisacrylamide (0.088 grams), sodium persul-  
fate (0.12 grams), and 2-hydroxy-2-methyl-1-phenyl-  
propan-1-one (0.034 grams) was prepared, then placed  
in shallow dish and polymerized under an ultraviolet  
lamp as set forth in Example 1 until the monomer  
25 mixture polymerizes into rubbery gel.

The gel was cut into small pieces then  
extruded through a KitchenAid Model K5SS mixer with a  
meat grinder attachment. The extruded gel then was  
dried in a forced-air oven at 120°C, ground, and

sized through sieves to obtain the desired particle size.

This resulting lightly crosslinked acidic resin contained 15 mole percent strong acid functionality ( $-\text{SO}_3\text{H}$ ) and 85 mole percent weak acid functionality ( $-\text{CO}_2\text{H}$ ).

#### EXAMPLE 6

##### Preparation of a Crosslinked Poly(vinyl alcohol-co-vinylamine) Resin

10 Poly(vinyl alcohol-co-vinylamine) (50 grams, 6 mol% vinylamine), available from Air Products Inc., Allentown, PA, was dissolved in 450 grams of deionized water in a glass jar to form a viscous solution. Ethylene glycol diglycidyl ether  
15 (0.2 grams) was added to the viscous solution, with stirring. The jar then was covered and placed in a 60°C oven for 16 hours to yield a rubbery gel of a lightly crosslinked poly(vinyl alcohol-co-vinylamine).

20

#### EXAMPLE 7

##### Preparation of a Crosslinked Poly(vinylamine) Resin

To 2 liters of a 3% by weight aqueous poly(vinylamine) solution was added 0.18 g of ethylene glycol diglycidyl ether (EGDGE). The resulting  
25 mixture was stirred to dissolve the EGDGE, then the mixture was heated to about 60°C and held for one hour to gel. The gel was heated to about 80°C and

held until about 90% of the water was removed. The resulting gel then was extruded and dried to a constant weight at 80°C. The dried, lightly crosslinked poly(vinylamine) then was cryogenically milled to  
5 form a granular material.

#### EXAMPLE 8

##### Preparation of a Poly(DAEA)/Poly(AA) Multicomponent SAP (Poly(AA) Continuous Phase)

The undried, rubbery poly(AA) hydrogel  
10 prepared in Example 1 (133 grams) was cut into pieces and extruded through a KitchenAid Model K5SS mixer with meat grinder attachment. The gel then was mixed with 50 grams of the dry poly(DAEA) particles (<106 microns in size) prepared in Example 2. The result-  
15 ing mixture was extruded three times using the KitchenAid mixer, then dried in a 60°C forced-air oven for 16 hours and finally ground and sized through sieves to obtain the desired particle size. The process yielded 83 grams of multicomponent SAP  
20 particles comprising poly(DAEA) microdomains dispersed in a continuous poly(AA) phase, and having a weight ratio of poly(DAEA) to poly(AA) of about 60/40.

EXAMPLE 9

Surface Treatment of the Poly(DAEA)/  
Poly(AA) Multicomponent SAP of Example 8

5 A surface-treating solution was prepared by  
admixing 0.15 grams EGDGE, 7.88 grams propylene  
glycol, and 1.97 grams deionized water until homoge-  
neous. Ten grams of the poly(DAEA)/poly(AA) multi-  
component SAP of Example 8 were placed in a beaker  
fitted with a vertical shaft stirrer. The dry multi-  
10 component SAP was stirred at a sufficient speed to  
fluidize the SAP in the beaker, then 0.4 grams of the  
surface-treating solution was added to the fluidized  
SAP dropwise via syringe. Then, stirring was  
stopped, and the beaker was placed in a 125°C forced-  
15 air oven for one hour to yield a poly(DAEA)/poly(AA)  
multicomponent SAP surface treated with 600 ppm of  
EGDGE.

EXAMPLE 10

20 Preparation of a Poly(AA)/Poly(DMAPMA)  
Multicomponent SAP (Poly(DMAPMA) Continuous Phase)

The poly(DMAPMA) hydrogel prepared in  
Example 3 (70 grams) was cut into pieces and extruded  
through a KitchenAid Model K5SS mixer with meat  
grinder attachment. The gel then was mixed with 32  
25 grams of dry poly(AA) particles (<106 microns in  
size) prepared in Example 1. The resulting mixture  
then was extruded three times using the KitchenAid  
mixer, followed by drying in a 60°C forced-air oven  
at 60°C for 16 hours, and finally grinding and sizing

through sieves to obtain the desired particle size. The process yielded 60 grams of multicomponent SAP particles comprising poly(AA) microdomains dispersed in a continuous poly(DMAPMA) phase, and having a  
5 poly(AA) to poly(DMAPMA) weight ratio of about 50/50.

#### EXAMPLE 11

##### Surface Treatment of the Poly(AA)/ Poly(DMAPMA) Multicomponent SAP of Example 10

A surface-treating solution was prepared by  
10 admixing 0.375 grams 1,8-dibromooctane and 9.625  
grams isopropanol until homogeneous. Ten grams of  
the poly(AA)/poly(DMAPMA) multicomponent SAP of  
Example 10 were placed in a beaker fitted with a  
vertical shaft stirrer. The dry multicomponent SAP  
15 was stirred at a sufficient speed to fluidize the SAP  
in the beaker, then 0.4 grams of the surface-treating  
solution was added to the fluidized SAP dropwise via  
syringe. Next, stirring was stopped, and the beaker  
was placed in a 105°C forced-air oven for one hour to  
20 yield a poly(AA)/poly(DMAPMA) multicomponent SAP  
surface treated with 1,500 ppm of 1,8-dibromooctane.

#### EXAMPLE 12

##### Poly(DAEA)/Poly(AA) Multicomponent SAP Prepared by Gel Coextrusion

25 Thirty grams of the poly(DAEA) of Example 2  
were extruded through a KitchenAid Model K5SS mixer  
with meat grinder attachment. Twenty-four grams of  
the poly(AA) hydrogel of Example 1 also were extruded

through a KitchenAid Model K5SS mixer with meat grinder attachment. The two extrudates then were combined via hand mixing, followed by extruding the resulting mixture two times using the meat grinder.

5 The extruded product then was dried for 16 hours at 60°C, milled and sized to 180-710 microns, and finally surface treated with 200 ppm EGDGE (as described in Example 9). The procedure yields multi-  
10 component SAP containing microdomains of poly(DAEA) and poly(AA), and having poly(DAEA)/poly(AA) weight ratio of about 60/40.

### EXAMPLE 13

#### Preparation of Poly(vinylguanadine) (Poly(VG))

To 500 ml of an aqueous solution of poly-  
15 (vinylamine) (1.98% solids, 93% hydrolyzed) was added 38.5 ml of 6M hydrochloric acid and 9.65g of cyanamide ( $H_2NCN$ ). The resulting solution was heated under reflux for 8 hours. The solution next was diluted to a volume of 3L (liters) with a 5% sodium  
20 hydroxide solution, then ultrafiltered ( $M_w$  cut off of 100,000) with 15L of a 5% sodium hydroxide solution, followed by 15L of deionized water. The resulting product was concentrated to a 2.6% solids solution, having a pH 11.54. A poly(vinylamine) solution has a  
25 pH 10.0. The 2.6% solids solution gave a negative silver nitrate test, and a gravimetric analysis of the polymer, after the addition of HCl, gave the following composition: vinylguanidine 90%, vinyl-  
formamide 7%, and vinylamine 3%. Infrared analysis  
30 shows a strong absorption at  $1651\text{ cm}^{-1}$ , which is not

present in poly(vinylamine), and corresponds to a C=N stretch.

#### EXAMPLE 14

##### Preparation of a Crosslinked Poly(VG) Resin

5           The 2.6% solids solution of Example 13 was further concentrated to 12.5% solids by distillation. To this 12.5% solids solution was added 1 mole % EGDGE, and the resulting solution then was heated in a 60°C oven for 5 hours to form a gel of lightly  
10 crosslinked poly(vinylguanidine).

#### EXAMPLE 15

##### Preparation of a Coextruded Poly(VG)/Poly(AA) Multicomponent SAP

15           The crosslinked poly(VG) hydrogel of Example 14 was coextruded with 1 mole equivalent of the poly(AA) of Example 1 by the method set forth in Example 12. A portion of the coextruded poly(VG)/-poly(AA) multicomponent SAP then was surface cross-linked with 200 ppm EGDGE, by the method set forth in  
20 Example 9.

EXAMPLE 16

PEI/Poly(AA) Coextruded Multicomponent  
SAP Prepared by Gel Coextrusion

5 Aqueous solutions containing 10% and 20% by  
weight polyethylenimine (PEI,  $M_w$  of 60,000, available  
commercially as EPOMIN P-1000, Aceto Corp., Lake  
Success, NY) were crosslinked with 1.0 and 1.5 mole %  
EGDGE by the method set forth in Example 6, i.e.,  
10 heating for 16 hours at 60°C, to provide rubbery  
gels. The rubbery PEI gels (37.4 wt.%) were coex-  
truded with the poly(AA) gel of Example 1 (62.6 wt.%)  
in accordance with the method set forth in Example  
12, and the resulting coextruded multicomponent SAPs  
were dried in an oven at 60°C. The dried multi-  
15 component SAPs were cryogenically milled, and then  
sized.

In the test results set forth below, the  
multicomponent SAP particles of the present invention  
were tested for absorption under no load (AUNL) and  
20 absorption under load at 0.28 psi and 0.7 psi (AUL  
(0.28 psi) and AUL (0.7 psi)). Absorption under load  
(AUL) is a measure of the ability of an SAP to absorb  
fluid under an applied pressure. The AUL was deter-  
mined by the following method, as disclosed in U.S.  
25 Patent No. 5,149,335, incorporated herein by refer-  
ence.

An SAP (0.160 g +/-0.001 g) is carefully  
scattered onto a 140-micron, water-permeable mesh  
attached to the base of a hollow Plexiglas cylinder  
30 with an internal diameter of 25mm. The sample is

covered with a 100 g cover plate and the cylinder assembly weighed. This gives an applied pressure of 20 g/cm<sup>2</sup> (0.28 psi). Alternatively, the sample can be covered with a 250 g cover plate to give an applied pressure of 51 g/cm<sup>2</sup> (0.7 psi). The screened base of the cylinder is placed in a 100mm petri dish containing 25 milliliters of a test solution (usually 0.9% saline), and the polymer is allowed to absorb for 1 hour (or 3 hours). By reweighing the cylinder assembly, the AUL (at a given pressure) is calculated by dividing the weight of liquid absorbed by the dry weight of polymer before liquid contact.

The following tables contain absorption and retention data for the multicomponent SAP particles of the present invention, for individual polymers present in the multicomponent SAP particles, and for simple admixtures of the dry resins present in the multicomponent SAP particles. The data shows a significant improvement in water absorption and retention for the present multicomponent SAP particles containing microdomains of an acidic and/or basic resin polymers within each particle compared to the individual resins and a simple admixture of the individual resins. The data in Tables 1-6 shows the improved ability of multicomponent SAP particles of the present invention to absorb and retain an aqueous 0.9% saline solution.

100-460360

Table 1

SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Poly(DAEA) alone <sup>1)</sup>	9.6	8.1	23.9	13.5	9.3	24.2
Polyacrylic Acid alone <sup>2)</sup>	11.9	10.8	14.3	12.0	10.8	14.3
SAP-1 <sup>3)</sup>	11.0	10.9	45.2	14.8	14.4	48.0
SAP-2 <sup>4)</sup>	12.5	9.6	26.7	18.9	13.1	30.1
SAP-3 <sup>5)</sup>	12.4	11.3	37.3	16.5	14.7	42.3
SAP-4 <sup>6)</sup>	20.1	17.2	28.6	24.7	20.7	34.1
SAP-5 <sup>7)</sup>	25.3	18.2	35.3	28.1	23	38.7
Multicomponent SAP-1 <sup>8)</sup>						
0 <sup>9)</sup>	23.7	16.3	41.6	26.9	20	41.7
200	26.7	24.7	41.2	27.1	25.1	39.9
400	27.3	24.1	43.4	27.5	24.5	44.0
600	29.2	23.8	41.8	29.5	24.0	41.2
800	26.6	24.1	40.9	26.7	24.2	41.7
1,000	27.5	24.3	39.9	27.8	24.2	40.7

Table 1

SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Multicomponent SAP-2 <sup>10)</sup>						
0 <sup>9)</sup>	26.3	15.4	40	26.9	17.3	39.4
400	26.5	20.5	39.3	27	22.4	40.3
600	27	18.3	40.2	27.1	20.7	40.6

- 1) particle size--180-710  $\mu$ m;
- 2) 0% neutralization, particle size--180-710  $\mu$ m, surface crosslinked--600 ppm EGDGE;
- 3) mixture of 60% poly(DAEA), particle sizes less than 180 nm, and 40% polyacrylic acid --0% neutralized;
- 4) mixture of 60% poly(DAEA), particle sizes less than 180 nm, and 40% polyacrylic acid --0% neutralized, crosslinked with 600 ppm EGDGE;
- 5) mixture of 60% poly(DAEA), particle size--180-710  $\mu$ m, and 40% polyacrylic acid --0% neutralized;
- 6) mixture of 60% poly(DAEA), particle size--180-710  $\mu$ m, and 40% polyacrylic acid --0% neutralized, crosslinked with 600 ppm EGDGE;
- 7) mixture of 60% poly(DAEA), particle sizes less than 180  $\mu$ m, and 40% polyacrylic acid--20% neutralized, particle size 180-710  $\mu$ m;
- 8) multicomponent SAP containing microdomains of poly(DAEA) (<180  $\mu$ m) as dispersed phase in poly(AA) (DN=0) continuous phase, poly(DAEA)/poly(AA) weight ratio--60/40;
- 9) ppm surface crosslinking with EGDGE; and
- 10) multicomponent SAP containing microdomains of poly(DAEA) (<180  $\mu$ m) as dispersed phase in poly(AA) (DN=20) continuous phase, poly(DAEA)/poly(AA) weight ratio--60/40.

103333 4605650

Table 2

SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Poly (DMPMA) <sup>(11)</sup>	10.2	8.6	18	11.4	10	18.3
Poly (DMPMA) <sup>(12)</sup>	9.3	5.2	17.4	11	6.9	17.8
Polyacrylic acid <sup>(13)</sup>	11.9	10.8	14.3	12.0	10.8	14.3
SAP-6 <sup>(14)</sup>	14.5	10.9	18.8	17.2	14.3	20.9
SAP-7 <sup>(15)</sup>	14	12	38.7	17.9	15.7	43.6
SAP-8 <sup>(16)</sup>	12.5	10.4	24.8	14.5	12.4	24.8
Multicomponent SAP-3 <sup>(17)</sup>						
0 <sup>9)</sup>	28.8	15	41.6	31	17.5	41.5
100	27.4	24.2	38.8	27.1	23.6	38.8
200	27.3	24.2	39.8	25.8	23	39
400	26	23	37	25.2	22.5	36.4
600	25.1	22.3	37.1	24.7	21.3	36.1
Multicomponent SAP-4 <sup>(18)</sup>						
0 <sup>9)</sup>	31.9	11.6	44.2	31.8	15.7	44.9
200	27.6	24.3	37.8	27.5	23.4	38.1
400	27.5	23.7	37.4	27.2	23.1	38.8

Table 2

SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Multicomponent SAP-5 <sup>19)</sup>						
O <sup>20)</sup>	23.6	12.9	37.9	25	14.4	38.5
1500	24.7	16.9	36.4	25.5	18.3	37.5

Polymers: Poly(DMAPMA), particle size less than 106  $\mu\text{m}$ ;

poly(DMAPMA), particle size 106-180  $\mu\text{m}$ ;

neutralized, surface crosslinked with 600 ppm EGDGE;

(14) mixture of 60% Poly(DMAPMA), particle size 106-180  $\mu\text{m}$ , and 40% polyacrylic acid-0% neutralized;

15 mixture of 60% Poly(DMAPMA), particle size <106  $\mu\text{m}$ , and 40% polyacrylic acid-0% neutralized;

16) mixture of 50% Poly (DMAPMA), and 50% polyacrylic acid-0% neutralized;

<sup>17)</sup> multicomponent SAP containing microdomains of poly(DMAPMA) (<106μm) as dispersed phase in poly(AA) (DN=0); continuous phase, poly(DMAPMA)/poly(AA) weight ratio 60/40;

18) multicomponent SAP containing microdomains of poly(DWAPMA) (106-180  $\mu\text{m}$ ) as dispersed phase in poly(AA) (DN=0) continuous phase, poly(DWAPMA)/poly(AA) weight ratio 60/40;

19) multicomponent SAP containing microdomains of poly(AA) (DN=0%) ( $<106\text{ }\mu\text{m}$ ) as dispersed phase in poly(DMAPMA) continuous phase, poly(AA)/poly(DMAPMA) weight ratio 50/50; and

20) ppm surface crosslinking with dibromooctane.

Table 3

SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Poly(vinylamine) alone	14.2	14.4	21.4	15	14.3	23.4
SAP-9 <sup>21)</sup>	21.2	18.6	28.3	23.8	20.5	36.3
Multicomponent SAP-6 <sup>22)</sup>						
0 <sup>21)</sup>	14.9	12.8	53.8	16.9	15.6	55.4
100	37.5	30.1	45.5	37.5	30.1	45.5
200	36.2	30.4	48.5	35.9	30.2	47.4
400	34.6	30.6	44.9	34.6	30.6	46.2

<sup>21)</sup> mixture of 37% poly(vinylamine) and 63% poly(AA); and

<sup>22)</sup> multicomponent SAP containing microdomains of poly(vinylamine) (<180  $\mu$ m) as dispersed phase in poly(AA) (DN=0) continuous phase, poly(vinylamine)/poly(AA) weight ratio--37/63.

Table 4

Coextruded Multicomponent SAP of Example 12  
(60/40 weight ratio poly(DAEA)/poly(AA))

Surface Treatment	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
0	30.5	13.3	41.1	30.6	16.3	40.2
200 ppm EGDGE	31	27.7	40.2	30.8	27.3	39.9

Table 5

SAP	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
Poly(vinylguanidine) hydro- chloride alone	21	16.1	31.2	22.4	18.0	32.7
Multicomponent SAP-7 <sup>23)</sup>						
0 <sup>9)</sup>	18.8	12.7	40.6	21.2	15.3	46.8
200	22	19.2	33.5	23.5	20.3	37.4

<sup>23)</sup> multicomponent SAP containing microdomains of poly(VG) and poly(AA), with a poly(VG)/poly(AA) weight ratio--  
50/50.

Table 6

PEI Gel (% Solids)	Cross- linker Level <sup>24</sup>	AUL (0.28 psi, 1 hr.)	AUL (0.7 psi, 1 hr.)	AUNL (1 hr.)	AUL (0.28 psi, 3 hr.)	AUL (0.7 psi, 3 hr.)	AUNL (3 hr.)
20	1.0	23	19.5	32	24.3	20.8	34.9
10	1.5	20.1	16.2	28.4	22.4	18.1	31.9

<sup>24)</sup> mole % EGDGE.

EXAMPLE 17

Preparation of a Multicomponent SAP Having  
a Poly(AA) Core Surrounded by a PEI Shell

Sorbitan monooleate (0.81 g) was dissolved  
5 in 200 ml of heptane. Ten grams of crosslinked, un-  
neutralized polyacrylic acid (180-425  $\mu$ m) was added  
to this solution to act as seed for the core/shell  
composite particles. The resulting mixture was  
stirred at 700 rpm with a paddle stirrer. Polyeth-  
10 yleneimine (PEI) (27.6 g, 30% in water,  $M_w=750,000$ )  
was added to the polyacrylic acid/heptane slurry,  
followed immediately by the addition of 3.6 g of  
EGDGE. The EGDGE and PEI were allowed to cure for  
4.5 hours at room temperature. The resulting SAP  
15 particles were allowed to settle, and the super-  
natant heptane was decanted. The SAP particles were  
rinsed three times with 100 ml of acetone. The SAP  
particles were allowed to dry overnight at room  
temperature, then further dried at 80°C for 2 hours  
20 to yield 23.43 g of the multicomponent SAP parti-  
cles.

The SAP particles of Example 17 then were  
tested for an ability to absorb synthetic urine  
under no load (AUNL) and under load (AUL) at 0.28  
25 psi and 0.7 psi, in accordance with the previously  
described method. The results are summarized below:

Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None	15.22	12.09	10.38	15.78	13.12	11.74

#### EXAMPLE 18

5        Preparation of a Multicomponent SAP Having a Poly(AA) Core Surrounded by a Poly(vinylamine) Shell

10                Sorbitan monooleate (1.88 g) was dissolved in 500 ml of heptane. Ten grams of crosslinked, unneutralized polyacrylic acid (180-425  $\mu$ m) was added to this solution to act as seed for the core/-shell composite particles. The resulting mixture was stirred at 700 rpm with a paddle stirrer. Poly-(vinylamine) (84 g, 10.67% in water,  $M_w > 100,000$ ) was added to the polyacrylic acid/heptane slurry,

15        followed immediately by the addition of 1.5 g of EGDGE. The EGDGE and poly(vinylamine) were allowed to cure for 6 hours at room temperature. The resulting SAP particles were allowed to settle, and the supernatant heptane was decanted. The SAP

20        particles were rinsed three times with 200 ml of acetone. The SAP particles were dried at 80°C for 3 hours to yield 17.89 g of the multicomponent SAP particles.

25                The SAP particles of Example 18 then were tested for an ability to absorb synthetic urine. The results are summarized below:

Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None	49.88	39.28	33.20	51.83	41.79	35.23

#### EXAMPLE 19

#### 5                    Preparation of a Multicomponent SAP                       Containing Agglomerated Poly(AA)                       and Poly(vinylamine)

                      An agglomeration solution containing the following ingredients was prepared:

- 10                    0.25 g EGDGE  
                       0.32 g Aluminum sulfate  
                       0.31 g Magnesium sulfate  
                       4.10 g Water  
                       15.0 g Propylene glycol.

- 15                    Under rapid agitation, 2.1 g of poly(vinylamine) (<180  $\mu$ m, 5 mole % crosslinked with EGDGE) and 2.38 g of poly(AA) (<180  $\mu$ m, 0.07 mole % crosslinked with MBA) were fluidized. With continued mixing, 0.84 g of the agglomeration solution was added to the  
 20                    fluidized powder blend. The resulting SAP particles were spread on a glass dish and dried at 125°C for 2.5 hours.

- The ability of the SAP particles to absorb and retain synthetic urine was determined. The  
 25                    results are summarized below:

Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None	55.09	40.40	31.22	56.71	41.01	37.80

#### EXAMPLE 20

5                    **Preparation of a Multicomponent SAP**  
                     **Comprising an Interpenetrating Polymer**  
                     **Network of Poly(AA) and Poly(vinylamine)**

10                    Reticulated poly(sodium acrylate) polymer  
                     beads (1.19 g) were acidified with 20 ml of 1M HCl,  
                     and allowed to stand for 1.5 hours. The poly(AA)  
                     beads then were filtered on a medium glass frit and  
                     rinsed with 50 ml of isopropyl alcohol. Air was  
                     drawn through the acidified poly(AA) beads for 0.5  
15                    hour to remove isopropyl alcohol from the pores of  
                     the poly(AA). The poly(AA) foam beads then were  
                     added to a premixed solution of 11.0 g of poly-  
                     (vinylamine) (10.67%,  $M_w > 100,000$ ) and 0.24 g of  
                     EGDGE. The resulting mixture coagulated and was  
                     allowed to cure for 2 hours at 60°C. The resulting  
20                    multicomponent SAP particles were spread on a dish  
                     and dried at 60°C overnight to yield 2.8 g of the  
                     agglomerated SAP particles. A portion of the re-  
                     sulting multicomponent SAP particles was annealed at  
                     125°C for 1 hour to effect surface crosslinking.  
25                    The remaining portion of the particles was not  
                     annealed. The ability of the IPN SAP particles of  
                     Example 20 were tested for an ability to absorb and

retain synthetic urine. The results are summarized below:

Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None			22.1			22.4
Annealing for 1 hr @ 125°C	32.8	25.2	21.7	34.	22.9	22.8

#### EXAMPLE 21

##### Preparation of a Multicomponent SAP Comprising a Layer of Poly(AA) in Laminar Contact with a Layer of Poly(vinylamine)

To 186 g of 5 wt% poly(AA) ( $M_w$  of about  $1.25 \times 10^6$ ) in water was added 1.18 g of EGDGE, and the viscous solution was mixed thoroughly. Separately, 106 g of poly(vinylamine) (10.67%,  $M_w$  >100,000) and 2.3 g of EGDGE were quickly mixed and spread on a 9" x 13" Teflon-coated metal sheet, then cured at 80°C for 10 minutes. Next, the poly(AA) solution was spread on the poly(vinylamine) gel and allowed to cure and dry at 80°C for 4 hours. The sheets shrunk during drying, and then the laminate was comminuted. A portion of the resulting multicomponent SAP particles was neither surface cross-linked nor annealed. A second portion was annealed at 125°C for 1 hour. A third portion was surface crosslinked with PG/H<sub>2</sub>O at 120°C in an identical manner as Example 19. The SAP particles of Example

21 were tested for an ability to absorb and retain synthetic urine. The results are summarized below:

Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
None	32.4	22.4	23.7	35.1	25.1	27
Annealed for 1 hr @ 125°C	25.3	20.1	22.1	29.1	21.7	24.4
Cross-linked with PG/H <sub>2</sub> O (80/20)	27	20.5	20.8	29.7	22.3	24.7

To demonstrate that a multicomponent SAP particle of the present invention can contain an acidic resin and/or a basic resin that is partially neutralized, a series of tests was performed on multicomponent SAP particles containing 45% by weight poly(AA) and 55% by weight poly(vinylamine). The multicomponent SAP particles were prepared as set forth in Example 12, but the percent neutralization of the poly(AA) and poly(vinylamine) was changed. The various multicomponent SAP particles were tested for an ability to absorb and retain synthetic urine, and the results are summarized in Table 7.

Table 7			
% Neutralized Poly(vinylamine)/ % Neutralized Poly(AA) (by weight)	Surface Crosslinking	AUL (0.7 psi, 1 hr)	AUL (0.7 psi, 3 hr)
0/0	None	16.8	21.6
0/10	None	13.4	16.9
0/25	None	12.6	16
10/0	None	37.2	37.7
25/0	None	24.4	25.3
10/10	None	19.2	24.3
25/25	None	19.8	19.3
50/50	None	11.9	13.8
0/0	PG/H <sub>2</sub> O <sup>25)</sup>	43.3	47.6
0/10	PG/H <sub>2</sub> O	34	36.9
0/25	PG/H <sub>2</sub> O	14.4	17.4
10/0	PG/H <sub>2</sub> O	30.9	31.4
25/0	PG/H <sub>2</sub> O	24.1	25.3
10/10	PG/H <sub>2</sub> O	39.3	41.2
25/25	PG/H <sub>2</sub> O	18.9	18.7
50/50	PG/H <sub>2</sub> O	12.1	14.5

<sup>25)</sup> Surface treatment with propylene glycol/water (80/20 ratio) as set forth in Example 19.

Additional tests were performed to illustrate that the acidic resin and/or basic resin of a multicomponent SAP particle can be partially neutralized. The various partially neutralized multicomponent SAP particles were tested for an ability to absorb synthetic urine. The results are summarized in Tables 8-11.

Table 8								
Sample	% Neut. PVam/PAA	AUL (0.28 1 hr.)	AUL (0.7 1 hr.)	AUNL (1 hr.)	AUL (0.28 3 hr.)	AUL (0.7 3 hr.)	AUNL (3 hr.)	
A	0/0	36	16.8	64.4	45.4	21.6	67.9	
B	0/10	20.5	13.4	68.4	23.4	16.9	69.4	
C	10/10	37	19.2	59.3	46.3	24.3	62.4	
D	10/0	40.4	37.2	50.2	40.6	37.7	51.4	
E	0/0	50.3	32	62.5	50.2	41.6	63.1	
F	0/25	19.9	12.6	63.4	22.7	16	63.7	
G	25/25	23.1	19.8	30.9	23	19.3	30	
H	25/0	28.2	24.4	38.6	29.7	25.3	42.2	
I	50/50	16.2	11.9	30.2	16.7	13.8	30.2	
J	0/0	50.8	43.3	62.9	55.1	47.6	68	
K	0/10	48.1	34	62	49.4	36.9	63.3	
L	10/10	44	39.3	54.3	46.4	41.2	58.7	

Table 8							
Sample	% Neut. PVam/PAA	AUL (0.28 1 hr.)	AUL (0.7 1 hr.)	AUNL (1 hr.)	AUL (0.28 3 hr.)	AUL (0.7 3 hr.)	AUNL (3 hr.)
M	10/0	35	30.9	45.3	36.4	31.4	45.9
N	0/0	48.7	42.6	59	50.1	44.2	61
O	0/25	27.9	14.4	63	31.1	17.4	64.7
P	25/25	26.7	18.9	35.1	22.2	18.7	28.4
Q	25/0	21.1	24.1	27.2	30	25.3	40.7
R	50/50	17.2	12.1	31.7	18.8	14.5	32.4

403280-160560

The multicomponent SAP particles tested in Table 8 contained (a) 55% by weight poly(vinylamine) (PVam) internally crosslinked with 2 mole % ethylene glycol diglycidyl ether (EGDGE) and (b) 45% by weight poly(acrylic acid) (PAA) internally cross-linked with 0.2 mole % methylene bis(acrylamide)-(MBA). The PVam and PAA, independently, were neutralized 0% to 50% weight percent. The multicomponent SAP particles of Samples A-I were not surface crosslinked. The multicomponent SAP particles of Samples J-R were annealed at 125°C.

Table 8 shows the ability of multicomponent SAP particles having the acidic resin and/or basic resin neutralized up to 50% by weight to absorb synthetic urine.

The following Table 9 includes AUL and AUNL data for multicomponent SAP particles containing 50% by weight unneutralized PVam and 50% by weight 30% neutralized PAA (DN=30). The multicomponent SAP contained varying amounts of EGDGE in the PVam resin and MBA in the PAA resin, as shown in Table 9. The multicomponent SAPs contained 50 wt% PVam and 50 wt% PAA. The data in Table 9 illustrates the ability of multicomponent SAP particles of the present invention to absorb synthetic urine.

Table 9						
Sample	EGDGE in PVam	MBA Level in PAA	AUL (0.7 1 hr.)	AUNL (1 hr.)	AUL (0.7 4 hr.)	AUNL (4 hr.)
A	1	0.2	18.1	63.2	21.3	62.8
B	1	0.4	40.8	58.8	40.7	57.2
C	1	0.8	39.6	56.5	39.6	56.3
D	1	1.2	34.8	51.7	35.4	52.9
E	2	0.2	15	65.9	18.5	65.7
F	2	0.4	16.8	61.5	21.8	60.9
G	2	0.8	33.3	51.7	33.5	50.1
H	2	1.2	31.6	46.8	30	47.1
I	4	0.2	15	64.4	19	65.3
J	4	0.4	17.1	58.8	22.4	58.9
K	4	0.8	36.4	51.7	37.1	51.1
L	4	1.2	28.6	46.2	29	44.8
M	6	0.2	15.2	60.1	18.8	61
N	6	0.4	16.6	56	20.5	55.8
O	6	0.8	33.3	48.7	33.8	47.4
P	6	1.2	29.5	43.8	29.3	42.4

Table 10 is similar to Table 9, except the multicomponent SAP particles contain 30% by weight unneutralized PVam and 70% by weight PAA (DN=30).

Table 10						
Sample	EGDGE in PVam	MBA Level in PAA	AUL (0.7 1 hr.)	AUNL (1 hr.)	AUL (0.7 4 hr.)	AUNL (4 hr.)
A	1	0.2	12.4	67.4	16.9	67.4
B	1	0.4	14.3	59.2	17.9	58.8
C	1	0.8	28.6	43.7	28.7	43
D	1	1.2	32.4	49	33.1	49
E	2	0.2	13.7	67.3	17.4	68.8
F	2	0.4	14.6	64	18.6	64.3
G	2	0.8	25.4	53.4	39.6	52.3
H	2	1.2	33.5	48.3	34.2	47.1
I	4	0.2	11.5	67.1	15.4	68.6
J	4	0.4	12.9	61.5	17	61.6
K	4	0.8	20.9	52.1	36.7	52
L	4	1.2	33.3	46.3	34.8	46.1
M	6	0.2	13	66.2	13	66.2
N	6	0.4	13	59.7	13	59.7
O	6	0.8	21.7	50.2	21.7	50.2
P	6	1.2	32.5	42.6	32.5	42.6

Tables 9 and 10 show that higher internal crosslinking levels, particularly in the PAA, provide multicomponent SAP particles having improved performance. The performance improves when both internal crosslinking levels are increased together, but good performance can be seen in the range of crosslinking levels listed in the tables. In Table 9, a preferred range of internal crosslinker for the PAA is about 0.2 to about 0.8 mole % MBA.

The results are even more illustrative in a lower amine formulation (i.e., 30 wt% PVam in the multicomponent SAP particle) of Table 10 wherein

enhanced performance is observed at an MBA internal crosslinker level in PAA of 0.8 mole%, with a preferred range of about 0.4 to about 1.2 mole% MBA. A preferred range for the amount of EGDGE internal crosslinker in PVam is about 1 to about 4, and preferably about 2 to about 4, mole percent.

Tables 11 and 12 show that increasing the cure time at 125°C had no effect on the performance of a multicomponent SAP containing PAA 30 mole% neutralized and unneutralized PVam. However, increasing cure temperature did improve the absorbance performance in 0.7 psi AUL tests. These results are shown in the tables below.

Table 11						
50/50 Blend PVam/PAA DN=30						
Sample	Time	Temperature (°C)	AUL (0.7 1 hr.)	AUNL (1 hr.)	AUL (0.7 4 hr.)	AUNL (4 hr.)
A	2 hrs.	125	14.8	66.5	18.4	67
B	3 hrs.	125	16.1	65.6	19.8	65.9
C	5 hrs.	125	14.2	64	17.9	64.1
D	2 hrs.	140	16.2	65.1	20	65.2
E	2 hrs.	150	22.8	61.2	28.1	61
F	2 hrs.	160	29.4	58.2	34.8	57.7

Table 12						
30/70 Blend PVam/PAA DN=30						
Sample	Time	Temperature (°C)	AUL (0.7 1 hr.)	AUNL (1 hr.)	AUL (0.7 4 hr.)	AUNL (4 hr.)
G	2 hrs.	125	12.8	70.8	16.6	72.6
H	3 hrs.	125	13.1	70.8	17.1	72.3
I	5 hrs.	125	13.2	69.4	17.5	70.8
J	2 hrs.	140	13.5	68.6	17.1	69.9
K	2 hrs.	150	13.1	63.8	17.2	65.2
L	2 hrs.	160	14.8	60.7	20.2	61.6

5  
10 Tables 11 and 12 show preferred drying temperatures and times are greater than 150°C and/or for longer than 2 hours for the 50/50 PVam/PAA weight ratio, and greater than 160°C for the 30/70 PVam/PAA ratio.

15 In another series of tests, the ratio of acidic water-absorbing resin to basic water-absorbing resin in the multicomponent SAP particles was varied. In particular, Table 13 summarizes the AUNL data and the AUL data at different pressures for a series of multicomponent SAP particles containing  
20 poly(vinylamine) and poly(AA) over the range of 25% to 75% by weight. The multicomponent SAP particles used in this series of tests were prepared in accordance with the multicomponent SAP particles prepared in Example 12, and contained 55% by weight  
25 poly(vinylamine) and 45% by weight poly(acrylic acid). All multicomponent SAP particles used in the test were surface crosslinked with 50 ppm EGDGE.

The multicomponent SAP particles were tested for an ability to absorb and retain synthetic urine.

0903094-0320  
102280-160500

Table 13

Weight Ratio Poly(vinyl amine)/- Poly(AA)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUL 1.4 psi (1 hr)	AUNL (1 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)	AUL 1.4 psi (3 hr)	AUNL (3 hr)	AUL 0.28 psi (17 hr)	AUL 0.7 psi (17 hr)	AUL 1.4 psi (17 hr)	AUNL (17 hr)
25/75	41.3	36.6		53.6	41.2	36.6		54	39.1	33.3		52.3
30/70	46.3	42.2		58.7	46.4	42.8		59.6	43.1	38.7		58.4
35/65	43.6	38.5		54.4	44.2	39.5		54.8	42	35.8		54.3
40/60	52.1	44.3		63.9	53.7	46.5		66.7	51.7	43.2		65.2
45/55	50.4	46		61.1	51.4	47.4		63.2	47.3	41.9		61.9
50/50	52.2	45	26	62.5	54.8	47.7	29	66.7	52.8	45.4	30.9	66.4
55/45	52.1	47.3	27.4	62.5	54.8	49.3	31.3	66.2	53.1	44.8	32.5	65.4
60/40	52.8	47	27.8	64.6	55.2	49.6	30.9	68	52.6	44	33	67.6
65/35	50	45.9		59.2	51.6	47.3		61.8	48.8	41		61.4
70/30	47.5	43.1		57.4	48.3	43.8		59.4	43.5	37.2		56.7
75/25	43.9	39.3		53.6	43.9	39.2		54.8	38.9	31.2		51.4

In another series of tests, multicomponent SAP particles containing 45% poly(AA) and 55% poly-(vinylamine) by weight were prepared as set forth in Example 12. The multicomponent SAP particles were  
5 prepared by extruding the blended gels of acidic resin and basic resin using a KitchenAid mixer (as a control), or using a Brabender twin screw extruder containing both mixing and conveying elements. In some tests, additional back pressure was provided by a  
10 breaker plate and/or a screen. The speed of the Brabender extruder was varied. Both untreated and surface treated (i.e., PG/H<sub>2</sub>O 80/20) multicomponent SAP particles were tested. The various samples were tested for an ability to absorb synthetic urine. The results,  
15 summarized in Table 14, show that the more intimate blending provided by the Brabender extruder improved the absorption and retention properties of the SAP particles.

Table 14

Method of Extrusion	Surface Treatment	AUNL (1 hr)	AUL 0.28 psi (1 hr)	AUL 0.7 psi (1 hr)	AUNL (3 hr)	AUL 0.28 psi (3 hr)	AUL 0.7 psi (3 hr)
KitchenAid (control)	None	69.6	33	15.4	73.3	39.3	21.7
Brabender-no plate 25 rpm	None	71.4	41.7	13.9	74.7	46.6	19.6
Brabender-no plate 100 rpm	None	70.7	43.5	15.5	73.8	56.2	23.6
Brabender-plate 25 rpm	None	72	46.7	16	74.1	55.1	22.1
Brabender-plate 100 rpm	None	70.5	48.4	16.9	72.6	60	23.2
Brabender-plate 150 rpm	None	69.7	50.5	29.5	72.1	59.3	35.4
Brabender-plate 40 mesh screen 25 rpm	None	70.5	54.4	16.3	73.3	59.7	23.9
Brabender-plate 40 mesh screen 150 rpm	None	68.9	57.7	33.2	69	59.9	42.1
KitchenAid (control)	PG/H <sub>2</sub> O 80/20	64.3	51.9	40.3	69.9	55.7	44
Brabender-no plate 25 rpm	PG/H <sub>2</sub> O 80/20	66.2	53.7	42	70.4	56.9	44.6
Brabender-no plate 100 rpm	PG/H <sub>2</sub> O 80/20	65.4	52.8	41.6	68.8	56.1	45.4
Brabender-plate 25 rpm	PG/H <sub>2</sub> O 80/20	66.8	53.7	42.3	70.4	56.9	45.5
Brabender-plate 100 rpm	PG/H <sub>2</sub> O 80/20	66	53	44	68.8	55.5	47.6
Brabender-plate 150 rpm	PG/H <sub>2</sub> O 80/20	65.5	52.3	44.6	67.8	54.5	47.2
Brabender-plate 40 mesh screen 25 rpm	PG/H <sub>2</sub> O 80/20	65.2	54	45.6	68.3	56.2	49.1
Brabender-plate 40 mesh screen 150 rpm	PG/H <sub>2</sub> O 80/20	63.5	50.7	44.2	64.9	53.1	47.1

In addition to an ability to absorb and retain relatively large amounts of a liquid, it also is important for an SAP to exhibit good permeability, and, therefore, rapidly absorb the liquid.

5 Therefore, in addition to absorbent capacity, or gel volume, useful SAP particles also have a high gel strength, i.e., the particles do not deform after absorbing a liquid. In addition, the permeability or flow conductivity of a hydrogel formed when SAP  
10 particles swell, or have already swelled, in the presence of a liquid is extremely important property for practical use of the SAP particles. Differences in permeability or flow conductivity of the absorbent polymer can directly impact on the ability of an  
15 absorbent article to acquire and distribute body fluids.

Many types of SAP particles exhibit gel blocking. "Gel blocking" occurs when the SAP particles are wetted and swell, which inhibits fluid  
20 transmission to the interior of the SAP particles and between absorbent SAP particles. Wetting of the interior of the SAP particles or the absorbent structure as a whole, therefore, takes place via a very slow diffusion process, possibly requiring up  
25 to 16 hours for complete fluid absorption. In practical terms, this means that acquisition of a fluid by the SAP particles, and, accordingly, the absorbent structure, such as a diaper, can be much slower than the rate at which fluids are discharged,  
30 especially in gush situations. Leakage from an absorbent structure, therefore, can occur well before the SAP particles in the absorbent structure are

fully saturated, or before the fluid can diffuse or wick past the "gel blocked" particles into the remainder of the absorbent structure. Gel blocking can be a particularly acute problem if the SAP particles lack adequate gel strength, and deform or spread under stress after the SAP particles swell with absorbed fluid.

Accordingly, an SAP particle can have a satisfactory AUL value, but will have inadequate permeability or flow conductivity to be useful at high concentrations in absorbent structures. In order to have a high AUL value, it is only necessary that the hydrogel formed from the SAP particles has a minimal permeability such that, under a confining pressure of 0.3 psi, gel blocking does not occur to any significant degree. The degree of permeability needed to simply avoid gel blocking is much less than the permeability needed to provide good fluid transport properties. Accordingly, SAPs that avoid gel blocking and have a satisfactory AUL value can still be greatly deficient in these other fluid handling properties.

Accordingly, an important characteristic of the multicomponent SAP particles of the present invention is permeability when swollen with a liquid to form a hydrogel zone or layer, as defined by the Saline Flow Conductivity (SFC) value of the SAP particles. SFC measures the ability of an SAP to transport saline fluids, such as the ability of the hydrogel layer formed from the swollen SAP to transport body fluids. A material having relatively high SFC value is an air-laid web of woodpulp

fibers. Typically, an air-laid web of pulp fibers (e.g., having a density of 0.15 g/cc) exhibits an SFC value of about  $200 \times 10^{-7} \text{ cm}^3\text{sec/g}$ . In contrast, typical hydrogel-forming SAPs exhibit SFC values of  
5  $1 \times 10^{-7} \text{ cm}^3\text{sec/g}$  or less. When an SAP is present at high concentrations in an absorbent structure, and then swells to form a hydrogel under usage pressures, the boundaries of the hydrogel come into contact, and interstitial voids in this high SAP  
10 concentration region become generally bounded by hydrogel. When this occurs, the permeability or saline flow conductivity properties in this region is generally indicative of the permeability or saline flow conductivity properties of a hydrogel  
15 zone formed from the SAP alone. Increasing the permeability of these swollen high concentration regions to levels that approach or even exceed conventional acquisition/distribution materials, such as wood pulp fluff, can provide superior fluid  
20 handling properties for the absorbent structure, thus decreasing incidents of leakage, especially at high fluid loadings.

Accordingly, it would be highly desirable to provide SAP particles having an SFC value that  
25 approaches or exceeds the SFC value of an air-laid web of wood pulp fibers. This is particularly true if high, localized concentrations of SAP particles are to be effectively used in an absorbent structure. High SFC values also indicate an ability of  
30 the resultant hydrogel to absorb and retain body fluids under normal usage conditions.

The SFC value of the present multicomponent SAP particles are substantially improved over the SFC value for a standard poly(AA) SAP, as illustrated in the data summarized in Table 15. A  
5 method for determining the SFC value of SAP particles is set forth in Goldman et al. U.S. Patent No. 5,599,335, incorporated herein by reference.

102333 16052660

Table 15

	Sample 1 (Control) <sup>26)</sup>	Sample 2 (Comparative) <sup>27)</sup>	Sample 3 <sup>28)</sup>	Sample 4 <sup>29)</sup>	Sample 5 <sup>30)</sup>	Sample 6 <sup>31)</sup>	Sample 7 <sup>32)</sup>
Time (min)	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi	AUL 0.7 psi
0	0	0	0	0	0	0	0
5	25.3	14.8	26	26.3	17.8	19.3	13.6
10	30.7	20.9	33.2	34.5	23.4	20.4	16.2
15	32.1	25.1	37.9	38.8	26.3	21	17.4
30	33.8	31.2	43.3	44.1	29.9	20.8	17.6
45	34.2	34.3	45.8	45.6	31.8	21.6	19.3
60	34.5	36.4	47.6	46.2	32.4	21.7	20.1
120	35.2	40	49.1	47.6	33.6	22.3	20.5
180	35.2	42.3	49.7	48	35.6	22.8	21.7
SFC <sup>33)</sup>	15	115	368	685	707	534	930

<sup>26)</sup> Standard, commercial SAP, i.e., neutralized poly(AA), 75% DN, available as A2300, from Chendal, Corp., Palatine, IL;

<sup>27)</sup> Comparative sample containing a dry blend of 55% by weight unneutralized poly(vinylamine) particles and 45% by weight unneutralized poly(AA) particles;

<sup>28)</sup> Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 55% poly(AA), prepared in a KitchenAid mixer in accordance with Example 12;

<sup>29)</sup> Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 12;

- 30) Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 18;
- 31) Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 20;
- 32) Multicomponent SAP particles of the present invention, containing 55% unneutralized poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 21; and
- 33) in  $\times 10^{-7}$  cm<sup>3</sup>sec/g.

002280-460560

The data summarized in Table 15 shows a substantial improvement in AUL at 0.7 psi and SFC for multicomponent particles of the present invention in comparison to a control SAP and a comparative dry blend of SAP particles. Accordingly, a present multicomponent SAP particle has an SFC value of at least about  $150 \times 10^{-7}$  cm<sup>3</sup>sec/g, and preferably at least about  $250 \times 10^{-7}$  cm<sup>3</sup>sec/g. To achieve the full advantage of the present invention, the SFC value is at least about  $350 \times 10^{-7}$  cm<sup>3</sup>sec/g, and can range to greater than  $1000 \times 10^{-7}$  cm<sup>3</sup>sec/g.

The present multicomponent SAP particles also exhibit excellent diffusion of a liquid through and between the particles. FIG. 8 contains plots of Performance Under Pressure (PUP) capacity at 0.7 psi over time for a dry blend of 55% unneutralized poly(vinylamine) and 45% unneutralized poly(AA), for a standard commercial poly(AA) SAP, and for a present multicomponent SAP. The PUP capacity test is similar to the AUL test, but the SAP particles are allowed to absorb a fluid on demand. The PUP test is designed to illustrate absorption kinetics of an SAP particle.

In contrast, the plots of FIG. 8 illustrate that the present multicomponent SAP particles (i.e., 55/45 weight ratio unneutralized poly(vinylamine)/poly(AA) particles prepared using a Brabender extruder in accordance with Example 12 and annealed for 1 hour at 125°C) essentially attain their absorptive capacity after 1 hour, and have attained their absorptive capacity after 3 hours. The plots show that after 3 hours, the PUP capacity of the dry

blend has not been attained. The present multicomponent SAP particles, therefore, demonstrate a faster absorption of liquids, and a better diffusion rate of liquids into and through the particles, in addition to an ability to absorb and retain a greater amount of liquids than prior or other SAP products.

FIG. 8 also shows that a standard poly(AA) attains an absorptive capacity quickly, but does not absorb and retain as much of the electrolyte-containing liquid. Overall, FIG. 8 shows that the present multicomponent SAPs exhibit both a) improved absorption and retention, and b) improved permeability and absorption kinetics. Such results are both new and unexpected in the art.

FIG. 9 contains similar plots again showing improved absorption, retention, permeability, and absorption kinetics for a multicomponent SAP particle identical to those used in FIG. 8, except the particles tested in FIG. 9 were surface coated with 80/20 PG/H<sub>2</sub>O and heated at 125°C for 1 hour.

FIGS. 10 and 11 illustrate the improved initial performance under pressure (PUP) capacity rate for multicomponent SAP particles of the present invention. FIG. 10 shows the comparative initial PUP capacity rate for absorbency vs. (time)<sup>1/2</sup> for 16 hours between multicomponent SAP particles containing a 55/45 weight ratio of poly(vinylamine) and poly(acrylic acid) surface crosslinked with 80/20 PG/H<sub>2</sub>O, a dry blend of poly(vinylamine) and poly(acrylic acid), and a standard 75% neutralized poly(AA) SAP. The plots in FIG. 10 provide a better

measurement of the initial slope of the plots, and, therefore, provides a more meaningful comparison of initial PUP capacity rate.

5 The plots in FIG. 10 show a substantially improved initial PUP capacity rate for the multi-component SAP particles prepared using a KitchenAid mixer ( $93.2 \text{ g/g/hr}^{1/2}$ ) compared to a dry blend of SAP particles ( $40.7 \text{ g/g/hr}^{1/2}$ ) and to a standard poly(AA) ( $40.1 \text{ g/g/hr}^{1/2}$ ). FIG. 11 shows similar results for  
10 multicomponent SAP particles prepared in a Brabender extrusion apparatus and annealed for 1 hour at  $125^\circ\text{C}$ , i.e., initial PUP capacity of  $104.2 \text{ g/g/hr}^{1/2}$ .

A multicomponent SAP practice of the present invention, therefore, has an initial PUP  
15 capacity rate of at least  $50 \text{ g/g/hr}^{1/2}$ , and preferably at least  $70 \text{ g/g/hr}^{1/2}$ . To achieve the full advantage of the present invention, the multicomponent SAP particle has an initial PUP capacity rate of greater than  $90 \text{ g/g/hr}^{1/2}$ , and preferably greater  
20 than  $100 \text{ g/g/hr}^{1/2}$ .

In another test, the free swell rate (FSR) of a present multicomponent SAP particle was compared to the FSR of a standard poly(AA) SAP and 55/45 weight ratio of a poly(vinylamine)/poly-  
25 (acrylic acid) dry particle blend. The FSR test, also known as a lockup test, is well known to persons skilled in the art.

The present multicomponent SAP particles had an FSR (in  $\text{g/g/sec}$ ) of 0.49 and 0.48, for 55/45  
30 weight ratio multicomponent SAP particles made in a KitchenAid mixer and a Brabender extruder, respectively. In comparison, a dry blend had an FSR of

0.10 and a standard neutralized poly(AA) had an FSR of 0.32. Multicomponent SAP particles of the present invention, therefore, have an FSR of greater than 0.35, preferably greater than 0.40, and most preferably greater than 0.45. These data further show the improved ability of the present SAP particles to absorb and retain larger amounts of an electrolyte-containing liquid quickly.

The multicomponent SAP particles also can be mixed with particles of a second water-absorbing resin to provide an SAP material having improved absorption properties. The second water-absorbing resin can be an acidic water-absorbing resin, a basic water-absorbing resin, or a mixture thereof. The SAP material comprises about 10% to about 90%, and preferably about 25% to about 85%, by weight, multicomponent SAP particles and about 10% to about 90%, and preferably, about 25% to about 85%, by weight, particles of the second water-absorbing resin. More preferably, the SAP material contains about 30% to about 75%, by weight, multicomponent SAP particles. To achieve the full advantage of the present invention, the SAP material contains about 35% to about 75%, by weight, the multicomponent SAP particles. The multicomponent SAP particles can be prepared by any of the previously described methods, e.g., extrusion, agglomeration, or interpenetrating polymer network, and can be of any shape, e.g., granular, fiber, powder, or platelets.

The second water-absorbing resin can be any of the previously discussed acidic resins used in the preparation of a multicomponent SAP. The

second water-absorbing resin, either acidic or basic, can be unneutralized (DN=0), partially neutralized ( $0 < \text{DN} < 100$ ), or completely neutralized (DN=100). A preferred acidic water-absorbing resin used as the second resin is polyacrylic acid, preferably partially neutralized polyacrylic acid, e.g., DN about 50%, and preferably about 70% up to about 100%. The second water-absorbing resin also can be any of the previously discussed basic resins used in the preparation of a multicomponent SAP. Preferred basic water-absorbing resins used as the second resin are poly(vinylamine) or a poly(dialkylamino-alkyl(meth)acrylamide. Blends of acidic resins, or blends of basic resins, can be used as the second water-absorbing resin. Blends of an acidic resin and a basic resin also can be used as the second water-absorbing resin.

To illustrate the improved absorption properties demonstrated by an SAP material comprising multicomponent SAP particles and particles of a second water-absorbing resin, mixtures of multicomponent SAP particles and partially neutralized (DN=70) polyacrylic acid (poly(AA)) particles were prepared. As used here and throughout the specification poly(AA) (DN=70) refers to a standard, commercial poly(AA) neutralized about 70% to about 80%, and poly(AA) (DN=0) refers to unneutralized poly(AA). The multicomponent SAP particles contain microdomains of poly(vinylamine) dispersed in poly(AA) (DN=0). The poly(vinylamine)/poly(AA) weight ratio of the multicomponent SAP particles was 55/45. The resulting SAP material was tested for an ability to

absorb synthetic urine under load at 0.7 psi, in accordance with the previously described method. The results are summarized below:

wt ratio <sup>1)</sup>	AUL 0.7 psi (1 hr.)	AUL 0.7 psi (3 hr.)	SFC ( $\times 10^{-7}$ cm <sup>3</sup> sec/g)
100/0	26.7	27.1	14
75/25	30.2	30.7	26
50/50	36.7	37.7	72
25/75	40.8	42.6	189
0/100	43.0	46.4	787

<sup>1)</sup> weight ratio of partially neutralized poly(AA) particles to multicomponent SAP particles.

The data presented above shows a substantial improvement in absorption properties achieved by an SAP material comprising a blend of multicomponent SAP particles and particles of a second water-absorbing resin over conventional, partially neutralized poly(AA). The improved results are more clearly demonstrated by comparing the data presented above to the data summarized in the following Table 16, which contains absorption under load data for various mixtures of acidic and basic water-absorbing resins that lack a multicomponent SAP.

Table 16			
Example	Blend Ratio <sup>5)</sup>	AUL 0.7 psi (1 hr)	AUL 0.7 psi (3 hr)
1 <sup>1)</sup>	75/25	27.1	28.9
1	50/50	30.9	33
1	25/75	35.9	40.2
2 <sup>2)</sup>	75/25	26.6	27.3
2	50/50	28.7	30.3
2	25/75	26.3	27.3
3 <sup>3)</sup>	75/25	25.3	26
3	50/50	21.3	22.8
3	25/75	15.7	16.4
4 <sup>4)</sup>	55/45	37	45.2

<sup>1)</sup> Blend of (a) partially neutralized poly(AA) (DN=70) and (b) a mixture containing 55% by weight poly(vinylamine) and 45% by weight poly(AA) (DN=0);

<sup>2)</sup> Blend of (a) partially neutralized poly(AA) (DN=70) and (b) poly(vinylamine);

<sup>3)</sup> Blend of (a) partially neutralized poly(AA) (DN=70) and (b) poly(AA) (DN=0);

<sup>4)</sup> Blend of (a) poly(vinylamine) and (b) poly(AA) (DN=0); and

<sup>5)</sup> Weight ratio of (a) to (b) in each blend.

Table 17 contains additional AUL data at 0.7 psi showing the substantially improved absorption properties and SFC for blends containing particles of a multicomponent SAP. In particular, the data in Table 17 shows that an SAP material comprising a blend of multicomponent SAP particles and particles of a second water-absorbing resin (i.e., Samples 5-7) greatly outperformed a standard poly-

5

Table 17

Time (min)	Sample 1 (control) <sup>26)</sup>	Sample 2 (compara-tive) <sup>27)</sup>	Sample 3 (compara-tive) <sup>34)</sup>	Sample 4 (compara-tive) <sup>28)</sup>	Sample 5 <sup>35)</sup>	Sample 6 <sup>36)</sup>	Sample 7 <sup>37)</sup>	Sample 8 <sup>38)</sup>
0	0	0	0	0	0	0	0	0
5	25.3	14.8	16.4	26	21.7	28.3	27.5	24.4
10	30.7	20.9	23.5	33.2	26.8	34.7	33.6	30.2
15	32.1	25.1	26.8	37.9	30.4	37.8	36.2	32.8
30	33.8	31.2	31.2	43.3	36.9	42.5	39.8	36.5
45	34.2	34.3	33.4	45.8	39.5	44.6	41.9	38.1
60	34.5	36.4	34.8	47.6	42.7	45.9	43.3	38.9
120	35.2	40.0	36.1	49.1	48.7	48.2	46.7	40.1
180	35.2	42.3	37.3	49.7	50.1	50.4	48.4	46.4
SFC	15	115	59	368	194	207	244	179

<sup>34)</sup> Comparative sample containing a dry blend of 25% poly(AA) (DN=70), 41.5% poly(vinylamine), and 33.5% poly(AA) (DN=0);

<sup>35)</sup> SAP material containing 10% poly(vinylamine) and 90% multicomponent SAP containing 55% poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 12;

<sup>36)</sup> SAP material containing 10% poly(AA) (DN=0) and 90% multicomponent SAP containing 55% poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 12;

<sup>37)</sup> SAP material containing 11% poly(vinylamine), 9% poly(AA) (DN=0), and 80% multicomponent SAP containing 55% poly(vinylamine) and 45% poly(AA), prepared in accordance with Example 12;

<sup>38)</sup> Blend of 25% poly(AA) (DN=70) and 75% multicomponent SAP containing 55% poly(vinylamine) and 48% poly(AA), prepared in accordance with Example 12.

To further illustrate the improved absorption properties of an SAP material comprising a blend of (a) multicomponent SAP particles and (b) particles of a second water-absorbing resin, FIG. 12 contains plots of absorbance (g/g), both under load and not under load, for various combinations of poly(AA) (DN=70) and a multicomponent SAP containing 55% poly(vinylamine) dispersed in 45% poly(AA) (DN=0). The combinations tested in FIG. 12, which contain multicomponent SAP particles, outperformed the combinations tested in FIG. 13, which contain a blend of poly(AA) (DN=70), poly(AA) (DN=0), and poly(vinylamine) particles.

FIGS. 14-17 contain plots of absorbance (g/g) vs. time for various SAP materials and dry blends. FIG. 14 illustrates the absorption properties for a dry blend of poly(AA) (DN=70), poly(vinylamine), and poly(AA) (DN=0). The results in FIG. 14 are inferior to the results summarized in FIG. 15, which illustrate the absorption properties for an SAP material containing 80% multicomponent SAP, 11% poly(vinylamine), and 9% poly(AA) (DN=70). FIGS. 16 and 17 also show improved absorption properties for a blend of 90% multicomponent SAP and 10% poly(vinylamine) (FIG. 16) and for a blend of 90% multicomponent SAP and 10% poly(AA) (DN=0) (FIG. 17).

FIGS. 18 and 19 show that the present superabsorbent materials exhibit excellent permeability and absorption kinetics, in addition to excellent liquid absorption and retention. The plots in FIGS. 18 and 19 illustrate performance properties for a superabsorbent material containing,

by weight, 75% poly(AA) (DN=70) particles and 25% multicomponent SAP particles (55/45, by weight, poly(vinylamine)/poly(AA) (DN=0)). This superabsorbent material had an SFC of  $34.4 \times 10^{-7} \text{ cm}^3 \text{ sec/g}$ . FIG. 18 contains a plot of PUP at 0.7 psi over time. FIG. 18 demonstrates that a present superabsorbent material essentially attains its maximum absorption capacity after one hour (24.02 g/g). After 3 hours, the absorptive capacity was 24.74 g/g. After 16 hours, the absorptive capacity was 26.90 g/g.

The data presented above illustrates that a present SAP material has an SFC of greater than  $15 \times 10^{-7} \text{ cm}^3 \text{ sec/g}$ , and typically greater than  $20 \times 10^{-7} \text{ cm}^3 \text{ sec/g}$ . Preferred embodiments have an SFC about  $30 \times 10^{-7} \text{ cm}^3 \text{ sec/g}$  or greater, for example, up to about  $800 \times 10^{-7} \text{ cm}^3 \text{ sec/g}$ . In particular, an SAP material containing 25% multicomponent SAP particle and 75% poly(AA) (DN=70) particles has an SFC of  $34.4 \text{ cm}^3 \text{ sec/g}$ . An SAP material containing 75% multicomponent SAP particles and 25% poly(AA) (DN=70) has an SFC of  $189 \text{ cm}^3 \text{ sec/g}$ .

FIG. 19 illustrates the initial PUP capacity rate for absorbency vs.  $(\text{time})^{1/2}$  over 4 hours for a present SAP material. The plot in FIG. 19 demonstrates an improved initial PUP capacity rate of  $45.5 \text{ g/g } 1 \text{ hr}^{1/2}$  for the superabsorbent material. A standard poly(AA) (DN=70) has an initial PUP capacity rate of  $40.7 \text{ g/g } 1 \text{ hr}^{1/2}$ .

To further illustrate that the present multicomponent SAP particles and superabsorbent materials containing multicomponent SAP particles, (a) have an improved ability to absorb liquids faster, (b) have a better liquid diffusion rate, and

(c) have an improved ability to absorb and retain liquids, laboratory diaper cores containing the present multicomponent SAP particles were prepared and compared to laboratory diaper cores containing a  
5 conventional SAP and to commercially available diapers. In particular, the following the diaper cores were prepared:

- Core A - 100% poly(AA) (DN=70)
- 10 Core B - 100% multicomponent SAP particles containing 55% poly(vinylamine) and 45% poly(AA) (DN=0), by weight,
- Core C - 16.5% multicomponent SAP (as in Core B), 33.5% poly(AA) (DN=70), and 50% fluff pulp, by weight,
- 15 Core D - 23.3% multicomponent SAP (as in Core B), 46.7% poly(AA) (DN=70) and 30% fluff pulp, by weight,
- Core E - 33.5% multicomponent SAP (as in Core B), 16.5% poly(AA) (DN=70) and 50% fluff pulp, by weight,
- 20 Core F - 46.7% multicomponent SAP (as in Core B), 23.5% poly(AA) (DN=70) and 30% fluff pulp, by weight,
- Core G1 - 27.5% poly(vinylamine), 22.5% poly(AA) - (DN=0), and 50% fluff pulp, by weight,
- 25 Core G2 - identical to Core G1 except the multicomponent SAP was surface crosslinked with 500 ppm EGDGE,
- Core H1 - 38.5% poly(vinylamine), 31.5% poly(AA) - (DN=0), and 30% fluff pulp, by weight,
- 30

Core H2 - identical to Core H1 except the multicomponent SAP was surface-crosslinked with 500 ppm EGDGE.

5 Cores A and B are referred to as "pulp-less" cores, i.e., the cores contain 100% of an SAP. Typically, commercial diapers contain 45% to 60% by weight of a pulp to achieve rapid absorption of a liquid. Diaper Cores A through H2 were compared to one another, and to other laboratory cores and  
10 commercial diapers, to illustrate the improved permeability and absorption kinetics, and improved liquid absorption and retention, provided by a diaper having a core that contains multicomponent SAP particles of the present invention, either as  
15 the sole SAP, or as a component in a superabsorbent material.

Present day diapers generally consist of a topsheet made from a nonwoven material that is in contact with the skin of the wearer, an acquisition  
20 layer below (i.e., opposite the skin of wearer) the topsheet, a core that is below the acquisition layer, and a backsheet below the core. This construction is well known in the industry. In a preferred embodiment, the present diaper consists  
25 essentially of a topsheet, a core, and a backsheet, i.e., an acquisition layer is not present. As illustrated below, the improvements provided by present multicomponent SAP particles, or superabsorbent material, permit an acquisition layer to be  
30 omitted from a disposable diaper. Such a result is both new and unexpected in the art in that an expensive acquisition layer can be omitted, the diaper is

lighter and thinner, and absorptive properties are not adversely affected.

Cores A through H2, and the other laboratory cores referred to herein, were prepared using a  
5 conventional laboratory procedure as follows:

A laboratory core-forming unit comprising a two-chamber vacuum system forms an airlaid fluff pulp-absorbent composite matrix to produce a 12 cm x 21 cm diaper core. The core-forming unit comprises  
10 a roller brush on a variable-speed laboratory motor, a fiber distribution screen in close proximity to the brush, a forming screen on an adjustable damper, and a vacuum system capable of supplying a consistent and continuous negative pressure between 8 and  
15 15 inches of water.

The core-forming unit is contained such that the vacuum pulls the fibers and granular material from an adjustable introduction slide, through the rotating brush and distribution screen,  
20 directly onto the forming screen. The vacuum exhaust is recirculated through the inlet of the formation slide, thereby controlling the temperature and humidity of the operation.

When forming a core, the desired amount of  
25 defiberized fluff pulp is evenly disbursed in small pieces onto the brush roller in the upper chamber. In the lower chamber, a rectangular tissue, or top-sheet (21 cm x 12 cm), is placed onto the forming screen. For most cores, the sliding upper chamber  
30 lid is partially closed to leave about a one-half inch gap. In the case of a homogeneous pulp/SAP core, the SAP is sprinkled through the gap into the upper chamber immediately after the brush begins

rotating. In order to achieve a homogeneous distribution, a small amount of SAP is added to the fluff prior to beginning the motor. The amount of time used to introduce the remainder of the SAP  
5 varies with the amount of fluff pulp utilized. After the fiber and absorbent polymer material are deposited, the motor is turned off, and the damper unit containing the laboratory core is removed from the lower chamber. The uncompressed core then is  
10 placed on a backsheet made from a polymeric film, and put into a compression unit. At this time, another rectangular tissue and a nonwoven coverstock is placed on top of the core. Absorbent cores are compressed for a given amount of time, typically 5  
15 minutes, with a hydraulic press at pressures of between about 5,000 psi and about 10,000 psi, and typically about 7,000 psi, to achieve the desired density. After the 5 minutes, the laboratory-prepared absorbent cores are removed from the press,  
20 weighed, and measured for thickness.

Cores A through H2, and other laboratory cores and commercial diapers, were tested for rewet under a 0.7 psi load, liquid acquisition time, and liquid acquisition rate. The following describes  
25 the procedure to determine the acquisition and rewet under load of a hygienic article, like a diaper. These tests exhibit the rate of absorption and fluid retention of a 0.9%, by weight, saline solution, by a hygienic article over 3 to 5 separate fluid in-  
30 sults while under a load of 0.7 psi.

**Apparatus:**

- 100 ml separatory funnel, configured to deliver a  
flow rate of 7 ml/sec., or equivalent;  
3.642 kg circular weight (0.7 psi) 10 cm diameter,  
5 with 2.38 cm ID perspex dose tube through the center  
of weight;  
VWR Scientific, 9 cm filter paper or equivalent;  
2.5 kg circular weight (0.7 psi)--8 cm diameter;  
Digital timer;  
10 Electronic balance (accuracy of a 0.01 gram);  
Stopwatch.

**Procedure:**

**1. Preparation**

- 15 (a) Record the weight (g) of the hygienic  
article, e.g., diaper, to be tested;  
(b) Place hygienic article flat on the bench  
top, for example, by removing any elastics  
and/or taping the ends of the article to  
the bench top;  
20 (c) Place the 3.64 kg circular weight onto the  
hygienic article with the opening of the  
perspex dose tube positioned at the insult  
point (i.e., 5 cm toward the front from  
the center).

## 2. Primary Insult and Rewet Test

- 5 (a) Measure 100 ml of 0.9% NaCl solution  
(i.e., 0.9% by weight sodium chloride in  
deionized or distilled water) into separa-  
10 tory funnel. Dispense the NaCl solution  
into the perspex tube of the weight at a  
flow rate of 7 ml/sec and start the timer  
immediately. Stop the timer when all of  
the NaCl solution has completely dis-  
appeared from the surface of the hygienic  
article at the base of the perspex tube.  
Record this time as the primary acquisi-  
tion time (sec).
- 15 (b) After 10 minutes have elapsed, remove the  
weight and conduct the rewet test pro-  
cedure:
- 20 (i) Weigh a stack of 10 filter papers,  
record this value (dry weight).
- (ii) Place the filter papers over the  
insult point on the hygienic  
25 article. Set the timer for 2  
minutes. Place the 2.5 kg weight  
onto the filter papers and start  
timer immediately.
- (iii) After 2 minutes have elapsed, re-  
move the weight and reweigh the  
filter papers (wet weight). Sub-  
tract the dry weight of the filter  
papers from the wet weight, this is  
30 the rewet value. Record this value  
as the primary rewet value (g).

### 3. Secondary Insult and Rewet Test

- (a) Place the 3.64 kg weight back onto the hygienic article in the same position as before. Repeat step 2a using 50 ml NaCl solution (recoding the absorption time as the secondary acquisition time) and steps 2b (i)-(iii) using 20 filter paper (recording the rewet values as the secondary rewet).

### 4. Tertiary, and additional, Insult and Rewet Tests

- (a) Place the load back onto the diaper in the same position as before. Repeat step 2a using 50 ml of NaCl solution (recording the absorption time as the tertiary acquisition time) and steps 2b (i)-(iii) using 30 filter paper (recording the rewet value as the tertiary or subsequent rewet).

The following FIGS. 20-29 illustrate improved diapers that contain multicomponent SAP particles, or that contain superabsorbent materials, of the present invention.

FIG. 20 contains plots of acquisition time vs. number of insults with 0.9% aqueous saline, under a 0.7 psi load, for diapers containing Cores A and B, a core containing 50% of a multicomponent SAP and 50% fluff (Core N), a comparative core containing 50% poly(AA) (DN=70) and 50% fluff (Core I), a core identical to Core I, but absent an SAP (Core J), and a core identical to Core J but containing

twice the amount of fluff as Core J (Core K). In FIG. 20, Cores B and N are cores of the present invention. Cores A, I, J, and K are comparative cores.

5 Cores B and N exhibited an excellent ability to acquire 0.9% saline under a 0.7 psi load. Cores J and K acquired the saline slowly, especially during rewetting. Core I represents a standard core containing 50% SAP, and has a higher acquisition  
10 time than Cores B or C. The acquisition time for Core A could not be measured beyond the third insult because acquisition was very slow.

FIG. 21 illustrates the acquisition time under a 0.7 psi load for Cores I and N and for  
15 various commercial diapers. FIG. 21 shows that Core N, a core of the present invention, significantly outperforms both comparative laboratory cores (Core I) and commercial diapers with respect to acquisition time of 0.9% saline under a 0.7 psi load. FIG.  
20 22 illustrates that a core of the present invention, i.e., Core N, has a greater acquisition rate at 0.7 psi than commercial diapers and comparative laboratory cores containing poly(AA) (DN=70) (i.e., acquisition rate is greater than 2 ml/sec for an initial  
25 100 milliliter insult and four subsequent 50 milliliter insults with 0.9% saline).

FIG. 23 contains acquisition times for Cores B, D, and F, for a comparative core containing 70% poly(AA) (DN=70) and 30% fluff (Core L), and for  
30 a core containing 70% multicomponent SAP particles and 30% fluff (Core M). Cores B, D, F, and M of the present invention significantly outperformed Core L with respect to acquisition time. Core L could not

be tested for the fifth insult because the acquisition time was too great.

FIG. 24 similarly compared Cores C, E, I, and N. All cores contained 50% SAP, and Cores C, E, and N of the present invention significantly outperformed comparative Core I. FIG. 25 contains similar plots for cores containing 70% SAP. Cores D, E, and M significantly outperformed comparative Core L with respect to acquisition time.

FIGS. 26-29 contain plots of acquisition time and acquisition rate, and show that at both a 70% SAP loading of the core (FIGS. 26 and 27) and at a 50% SAP loading of the core (FIGS. 28 and 29), the cores of the present invention, i.e., cores G1, G2, H1, H2, M, and N, significantly outperformed comparative cores I and L.

Overall, the data presented in FIGS. 20-29 demonstrate that a diaper core of the present invention maintains a flat, essentially constant, or surprisingly a decreased, acquisition time over five insults, whereas prior cores demonstrate an increased acquisition time as the number of insults increase. The data also shows an unexpected faster acquisition rate as the number of insults increases, i.e., an acquisition rate for a subsequent insult is greater than for a previous insult. Such results are unexpected because prior cores exhibit a decrease in acquisition rate as the number of insults increase. The present cores, therefore, have second acquisition rates that are at most 20% slower than a first acquisition rate, and typically are 1%-20% slower, are equal to, or are greater than the first acquisition rate. The practical result of these

improved properties is a core having a greatly improved ability to prevent leakage in gush situations and in rewet situations, even in the absence of acquisition layers.

5           The data also shows that significant improvements in liquid absorption, both with respect to kinetics and retention, are observed if the standard poly(AA) (DN=70) presently used in cores is completely replaced by multicomponent SAP particles, or is replaced by a superabsorbent material of the present invention, i.e., a composition containing multicomponent SAP particles and a second water-absorbing resin, such as poly(AA) (DN=70).

10           The improved results demonstrated by a core of the present invention also permit the thickness of the core to be reduced. Typically, cores contain 50% or more fluff or pulp to achieve rapid liquid absorption while avoiding problems like gel blocking. The present cores, which contain a multicomponent SAP particles, acquire liquids sufficiently fast to avoid problems, like gel blocking, and, therefore, the amount of fluff or pulp in the core can be reduced, or eliminated. A reduction in the amount of the low-density fluff results in a thinner core, and, accordingly, a thinner diaper.

15           Therefore, a core of the present invention can contain at least 50% of an SAP, preferably at least 75% of an SAP, and up to 100% of an SAP. In various embodiments, the presence of a fluff or pulp is no longer necessary, or desired. In each case, the SAP in a present core contains multicomponent SAP particles, in an amount of about 15% to 100% of the SAP. The remaining SAP can be a second water-

absorbing resin, either basic or acidic. The second water-absorbing resin preferably is not neutralized, but can have a degree of neutralization up to 100%. The multicomponent SAP particles can be admixed with particles of a second water-absorbing resin for introduction into a diaper core. Alternatively, the diaper core can contain zones of multicomponent SAP particles and zones of a second water-absorbing resin.

In addition to a thinner diaper, the present cores also allow an acquisition layer to be omitted from the diaper. The acquisition layer in a diaper typically is a nonwoven or fibrous material, typically having a high degree of void space of "loft," that assists in the initial absorption of a liquid. The present cores acquire liquid at a sufficient rate such that diapers free of an acquisition layers are practicable.

Many modifications and variations of the invention as hereinbefore set forth can be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated by the appended claims.